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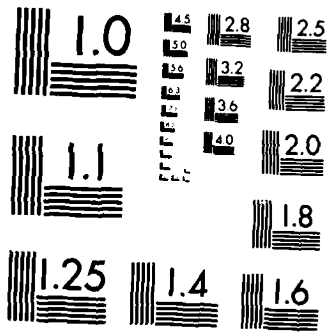
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Recycling Agent Selection and Tentative Specification

BADRU M. KIGGUNDU
BETTY NUSSER-HUMPHREY
DENNIS M. ZALLEN

NEW MEXICO ENGINEERING
RESEARCH INSTITUTE
Box 25
University of New Mexico
Albuquerque, New Mexico 87131

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This report summarizes a 2 1/2 year research effort toward developing a procedure by which a standard laboratory can define appropriate modifiers to recycle old paving-grade asphalt in hot central plant-recycling operations.

Literature reviews and discussions with expert asphalt chemists, technologists, research institutions, and oil companies were conducted. Field-aged asphalt cores from different climatic areas and modifiers were collected and characterized. Characterization using physical and chemical tests was performed on aged binders, modifiers, fresh and RTFO aged blends, and recovered recycled aged binders. Recycled Marshall mixtures were prepared and periodically characterized during accelerated oven aging. Chemical parameters identified were used to establish the laboratory test matrix. These parameters included the Polar/Saturate (P/S) ratio and percent generic aromatics as determined by a modified Clay-Gel (ASTM D2007) method. (over)

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The results indicate that some chemical and physical properties can be correlated and that modifier/aged asphalt compatibility can be assessed by chemical methods developed in this study. Finally, a tentative recycling agent selection specification has been developed, but more research is required for validation.

PREFACE

This report was prepared by the New Mexico Engineering Research Institute (NMERI), University of New Mexico at the Eric H. Wang Civil Engineering Research Facility, Kirtland Air Force Base, New Mexico, under Contract F29601-81-C-0013, Job Order 2104-1A29, for the Engineering and Services Laboratory, Headquarters, Air Force Engineering and Services Center, Tyndall Air Force Base, Florida 32405.

This report summarizes work performed between March 1982 through July 1984. Mr. James G. Murfee was the AFESC/RDCF Project Officer.

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This report has been reviewed by the Public Affairs Office and is releaseable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and approved for publication.

JAMES G. MURFEE
Project Officer

ROBERT E. BOYER, Col, USAF
Director, Engineering and
Services Laboratory

Everett L. Mabry

EVERETT L. MABRY, Lt Col, USAF
Chief, Engineering Research
Division

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SECTION I

INTRODUCTION

BACKGROUND

Recycling of asphalt pavements has increased in the United States to the point where it is common to find recycled materials in almost any paving job. With diverse location of installations throughout the world, the Air Force has found that the use of existing pavement materials represents a significant cost savings. Airfield pavements have unique service characteristics. Foremost among these are variable loads and tire pressure. In addition, most Air Force installations are located in remote areas, far from quality raw materials. Over 90 percent of the Air Force flexible pavement structures are beyond their design life. Worldwide, these cover an area in excess of 208 million square yards.

A number of products, marketed during the past several years, reportedly improve aged asphalt cements when introduced into aged asphalts during the recycling process. To date, only limited evidence exists to show that these products actually improve performance. There are only limited data on the physical and chemical properties of materials before and after hot central plant-recycling operations. Chemical and physical analyses are needed to determine (a) the effects of hot central plant-recycling operations on mixes; (b) how rejuvenators and soft asphalts affect aged asphalts, (c) what performance characteristics these recycled materials exhibit; and (d) a method to evaluate these parameters so they can be controlled to produce an optimum construction product.

The Air Force spent approximately 80 million dollars in FY 83 on the maintenance and repair of airfield pavements. An increasing number of these projects can reuse existing materials if adequate recycling specifications are available. It is estimated that significant cost savings, in some cases approaching 30 percent, could be realized with recycling. But recycling projects must be engineered with full knowledge of the best modifiers required to make the asphalt concrete perform predictably under aircraft loading. A tremendous increase in the use of recycling for Air Force projects is expected in the future. Thus, methods and criteria to specify the type of modifiers required is essential to Air Force rehabilitation and maintenance programs.

A valuable and useful technique used throughout the chemical field and widely applied to the study of asphalts is infrared spectroscopy (IR) (References 60-72). Infrared spectroscopy has been used to study hydrogen bonding in asphalts, effects of oxidation, effects of various solvents, asphalt fractions obtained by chemical separation, and the hardening process of asphalts. Petersen et al. (References 65, 66, and 67) used IR extensively to study oxidation products present in both laboratory and field-aged asphaltic materials. The technique provides information about the presence and concentration of functional groups such as ketones, carboxylic acids, anhydrides, etc. Changes upon oxidation and aging can then be studied. Although this technique is a powerful tool and has been used in much research, the instrumentation required is expensive and sample preparation is critical. Additionally, interpretation of the data requires a great deal of expertise.

Another method that was investigated for chemical analysis of asphalts and recycling agents is nuclear magnetic resonance (NMR). NMR has been used on a limited basis involving asphalt materials. Ramsey (Reference 73) determined structural parameters of whole asphalts, including

- relative number of aromatic carbon atoms,
- number of peripheral aromatic carbons, and
- carbon to hydrogen rations.

Al-Farkh et al. (Reference 74), Tewari, et al. (Reference 75), Corbett et al. (Reference 76), and Helm et al. (Reference 62) have used NMR to analyze asphalt and, in general, to estimate structural unit weights.* NMR requires expensive instrumentation as well as complex sample preparation; therefore, it is not widely used for routine analysis.

Selected Methods

The following criteria were developed by the New Mexico Engineering Research Institute as the basis for selecting chemical methods for use in this research effort. The methods chosen would

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*Additional information in this area has been provided by personal communications from R. H. Wombels, W. P. Jennings, and J. C. Petersen.

Heithaus method in recent studies. Results from the Heithaus technique could be used in defining compatibility between aged asphalt binders and modifiers.

The asphaltene solubility titration test is reported to have been developed by Bichard and modified by Waxman et al. (Reference 51). This method is similar to the Heithaus but differs primarily in data presentation and interpretation. Hildebrand (References 52, 53, and 54) is credited with development of the solubility parameter, however, it is difficult to measure with certainty. Other factors are also involved when trying to measure solubility. Therefore, the potential of the Heithaus or the asphaltene solubility titration tests in studying compatibility of modifiers with aged asphalts is considered great.

Plancher (Reference 24) and coworkers at the Western Research Institute (formerly the Laramie Energy Technology Center) adapted the asphaltene settling (rate) test to paving asphalts. The technique measures the ability of the asphaltenes to remain dispersed and is expressed in terms of settling time. The longer the settling time, the more stable the asphaltene structure, hence the more durable the asphalt. Although this test is considered simple, skill is required to obtain repeatable results (Reference 24).

High-Pressure Gel Permeation Chromatography (HP-GPC) is currently in use in an extensive research effort involving a number of states. HP-GPC (References 41, 55, and 56) was developed to analyze material of colloidal nature on the basis of molecular size. Jennings (References 41 and 55) has used HP-GPC on a number of materials including fresh asphalts, recovered aged asphalts, chromatographic fractions of asphalts, recycling agents and recycled blends. Jennings contends that a requirement of this technique is that one must obtain a "model" pavement, one that has had a service life in excess of 10 years. This "model" pavement is used to form a "model" chromatogram for the binder and is used as the basis for judging the performance characteristics of the binders being analyzed. Variation in the "model" chromatogram from region to region of the country is expected. The value of the large molecular size parameter (LMS) and the asphaltene content relative to the model is the basis for judging whether a pavement will perform well or not. Brule (References 57 and 58) and Kiet (Reference 59) have used HP-GPC to study asphalt fractions in varying concentrations and numbers.

where Vr = corrected retention volume. Davis et al. (Reference 46) adapted the IG-LC method to study oxidation effects in asphalts. In this same study, correlations were made between I_p determined with phenol as the test compound and durability results from nine asphalts. Davis and Petersen (Reference 47) established a linear correlation between I_p for phenol and the performance rating for asphalts from the Zaca-Wigmore Experimental Test Road. Poor field performance ratings as well as high-viscosity indices of asphalts correlated with high values of I_p. Although this technique offers a series of advantages, it has not yet been applied to the study involving evaluation of recycled asphalts.

The Heithaus Flocculation Ratio method (Reference 48) was developed to provide information about the solution properties of asphalts. This technique determines the peptizability of the asphaltenes (P_a), the peptizing power of maltenes (P_0), and the state of peptization of the system (P). The experimental results are presented graphically as Flocculation Ratio (FR) versus Dilution Ratio (DR) and FR versus $(DR)^{-1}$, where Flocculation Ratio is defined as

$$FR = \frac{\text{ml of polar solvent}}{\text{ml of (nonpolar + polar) solvent}} \quad (5)$$

and dilution ratio is defined as

$$DR = \frac{\text{ml of (nonpolar + polar) solvent}}{\text{grams of asphalt sample}} \quad (6)$$

From the plots of FR versus DR and FR versus $(DR)^{-1}$, the parameters, P_a, P_0, and P can be calculated (Reference 48). The larger the value of P_a, (asphaltene peptizability), the easier it is for the asphaltenes to remain dispersed. Additionally, Heithaus (Reference 48) and Van Kerkvoort (Reference 49) reported the P_a to be inversely proportional to the carbon/hydrogen (C/H) ratio of the asphaltenes and directly proportional to the C/H ratio of the maltenes, though nonlinearly. Other factors have also been noted to affect P_a and P_0. These include crude source, oxidation, refinery processes, cracking, concentration of asphaltenes and environment. Kemp et al. (Reference 50 and personal communication from D. A. Anderson) have utilized the

- A durability parameter has been proposed by Gannon and Co-researchers (Reference 34), and
- Most of the proposed specifications for recycling agents have based the compositional criteria on the Clay-Gel method.

Three additional methods were briefly investigated. They included the Silica-Gel Chromatographic method, the Boduszynski chemical separation method and the Kleinschmidt method. Griffin (Reference 37), O'Donnell (Reference 42), and Hibbard (Reference 43) have used the Silica-Gel method to separate asphalts and lubricating oils. The latter two methods have not been used to a great extent with aged asphalts and recycling agents.

Analytical Chemistry Techniques

The second category of chemical methods was designated as analytical methods for characterization of asphaltic materials. Under this category, a wide variety of analytical methods were investigated. They included inverse gas-liquid chromatography (IG-LC), Heithaus Flocculation Ratio method, asphaltene solubility titration test, asphaltene settling (rate) test, high-pressure liquid chromatography (HPLC), gel permeation chromatography (GPC), infrared spectroscopy (IR), nuclear magnetic resonance (NMR), elemental analysis, electron paramagnetic resonance (EPR), and some others that were identified as being of limited use to this study (Reference 44).

The inverse gas-liquid chromatography method was developed for characterizing asphalts by Davis, Petersen and Haines in 1966 (Reference 45). Basically the procedure involves a column composed of 1 part asphalt to 10 parts Fluoropak® 80 by weight. After conditioning, three reference n-paraffins were injected and retention volumes recorded. Then test compounds were injected and retention recorded. A parameter called the interaction coefficient, I_p, was then calculated. I_p is defined as

$$I_p = \left[\log_{10} V_r^0 \text{ (test compound)} - \log_{10} V_r^0 \begin{array}{c}\text{hypothetical}\\ \text{n-paraffin}\end{array}\right] \times 100$$

$$\log_{10} \frac{V_r^0 \text{ (test compound)}}{V_r^0 \text{ (hypothetical n-paraffin)}} \times 100 \qquad (4)$$

The Corbett-Swarbrick method (Reference 35) is an elution-absorption chromatographic technique involving the initial removal of the asphaltenes (A) by precipitation followed by the elution of three additional fractions: polar aromatics (P-A), naphthene-aromatics (N-A), and saturates (S).

Corbett (References 36, 37 and 38) reports that compositional analysis information can be used to differentiate asphalts, to study physical properties, to study effects of refinery processes as well as to investigate hardening. Although the Corbett method has been used in several studies (References 39, 40, 41, and personal communications from many experts) there are a limited number of users, and interlaboratory variability is reported to be large. This method was recently standardized by ASTM under designation D-4124.

The Clay-Gel adsorption chromatographic technique (ASTM, D2007-75) was developed by Houston Shell Laboratories primarily for evaluation of rubber extender oils. It involves the initial separation of the asphaltenes by precipitation with normal pentane followed by elution of three remaining fractions from two columns packed with silica gel and attapulgus clay. The latter three fractions are designated saturates, aromatics and polar aromatics.

Dunning and Mendenhall (Reference 6) have suggested the use of the Clay-Gel method for preliminary selection of recycling agents or modifiers. They also postulate that by using ASTM D341 temperature viscosity charts, a recycling agent with a minimum of 9 percent polars and 60 percent aromatics would be ideal to rejuvenate an aged asphalt. Kari and coauthors (Reference 33) recommended using the Clay-Gel procedure in recently proposed criteria for selection of a recycling agent. They also reported an excellent correlation between the saturate fractions obtained by the Rostler and the Clay-Gel methods.

Based on information from a variety of experts, the conclusion is that:

- The technique is simple and quick,
- Packaged column adsorbents are available,
- Some correlation with Rostler data has been reported (References 19, 33, and 34),
- There are fewer users in practice,
- It is a current standard (ASTM D-2007) during the life of this effort,

The Rostler-Sternberg method (Reference 28) uses an acid-extraction technique that separates the asphalt into five generic fractions: asphaltenes, nitrogen bases (N), first acidaffins (A_1), second acidaffins (A_2), and paraffins (P). Results (Reference 29) obtained by this method led to the formulation of a durability parameter defined as:

$$\text{Durability Parameter} = \frac{\text{Most Reactive Fractions}}{\text{Least Reactive Fractions}} \tag{2}$$

$$= \frac{N + A_1}{A_2 + P}$$

A compatibility parameter was also formulated and defined as

$$\text{Compatibility Parameter} = \frac{\text{Percent Nitrogen Bases}}{\text{Percent Paraffins}} = \frac{N}{P} \tag{3}$$

Rostler (References 19, 29, and 30) contends that the durability parameter predicts the performance characteristics of an asphalt. But experts contacted pointed out that the asphaltene fraction is not included in Rostler's durability parameter, yet the performance of a recycled binder depends upon the dispersibility of the asphaltenes.

Numerous studies (References 4, 10, 13, 19, 31, 32, 33 and 34) have used the Rostler-Sternberg method to establish fingerprinting files, to evaluate asphalts and recycling agents under various test conditions and to determine chemical composition of an extensive list of recycling agents, aged asphalts, and blended asphalts. Many agencies use the Rostler-Sternberg method because:

- A large data base is available,
- Its use is dictated by a client, and
- The method has been used for a long time.

However, the method was discontinued as an ASTM standard in the early 1970s. Reasons given by a variety of experts were the following:

- The adverse effects of an acid on the asphalt fractions,
- The method was developed for extender oils. The rubber industry lost interest in the method due to an observed interference of the asphaltenes in the other fractions,
- General decline in the user-producer demand, and
- The analysis time is quite long.

binders, modifiers, recycled blends and RTFO artificially aged blends. This effort culminates in the development of a tentative modifier or recycling agent selection specification.

In summary, the technology of recycling is fairly well developed for handling the component materials mechanically. Research work has been conducted and will continue toward an understanding of the chemical and physical characteristics of the components in binders and modifiers. There is only limited information on the chemical and physical properties of recycled asphaltic materials before and after hot central plant-recycling operations. A universally accepted principle in asphalt technology is that maintaining a high degree of asphaltene dispersion leads to highly durable pavement mixtures. Another well known viewpoint is that a high degree of asphaltene dispersion implies higher component compatibility. The concern for compatibility and/or asphaltene dispersion is more critical in recycling operations because the materials are generally of unknown origin. The techniques for measuring compatibility are not readily available. In attempting to develop criteria for a recycling agent selection, this research effort first searched for methods which can be used to characterize asphalts, modifiers and blends. Methods for measuring physical properties were also defined.

The following section provides a review of the chemical methods. At the end of that summary, the methods selected for this research effort will be outlined along with the criteria for the selections. A detailed discussion can be found in Reference 27.

Chemical Composition Techniques

Several chemical techniques were investigated before selecting the methods to be used in this research effort. They were classified into two categories: (1) generic compositional analyses methods, and (2) analytical methods for characterization of asphaltic materials.

In the first category, generic compositional analyses methods, six techniques were reviewed. These included the Rostler-Sternberg method, the Corbett-Swarbrick method, the Clay-Gel absorption chromatographic method, and, to a limited extent, the Silica-Gel chromatographic methods, the Boduszynski chemical separation method and the Kleinschmidt method.

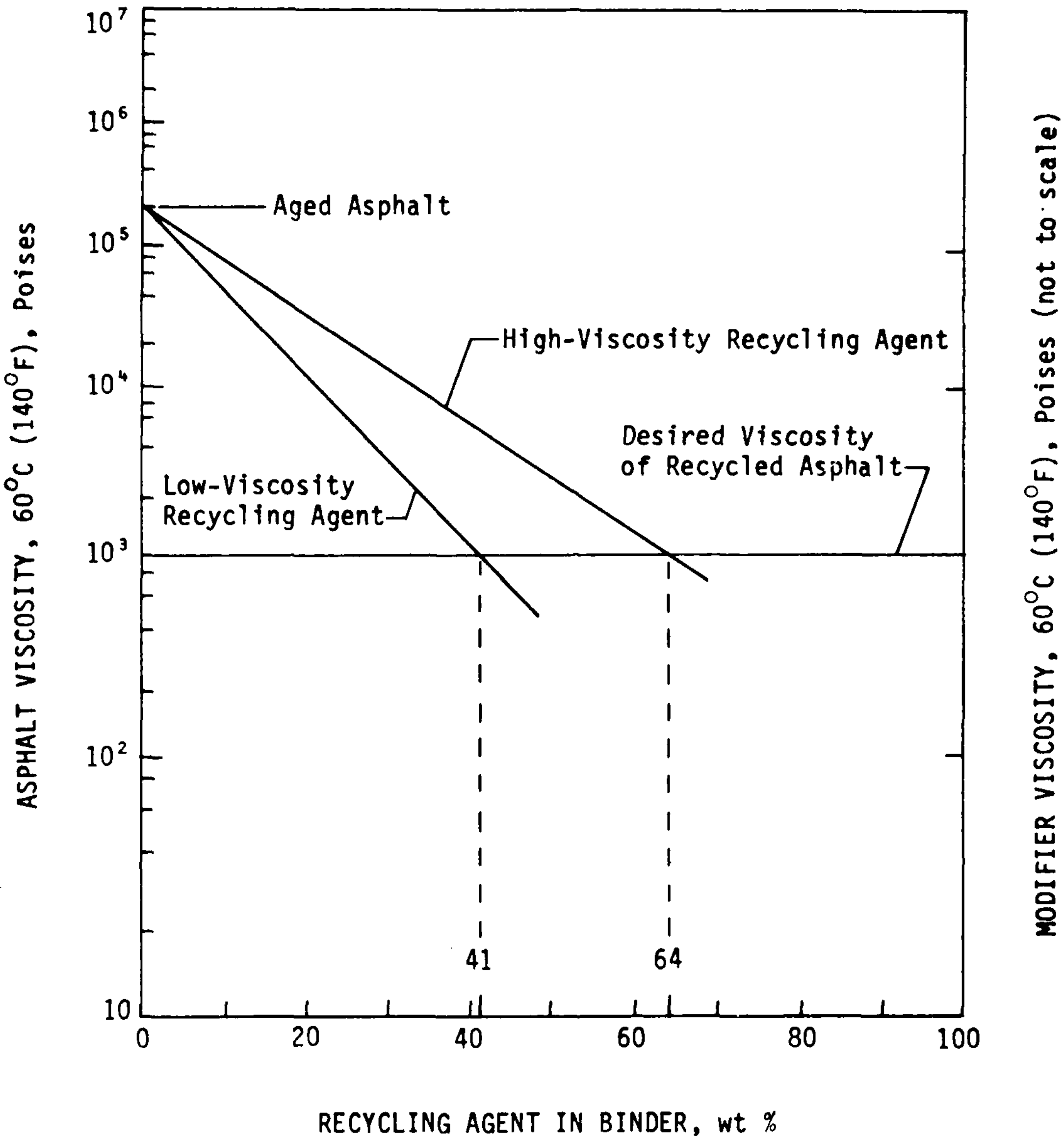

Figure 1. Percent Recycling Agent Required Depends on Viscosity (Reference 25).

selection of component parts and by providing an understanding of the observed performance differences in asphaltic materials of the same grade (or same physical specifications). Plancher et al. (Reference 24) developed an asphaltene dispersion test called the Asphaltene Settling Test. The rate at which the asphaltenes settle out of the solution is believed to provide some information on compatibility of the interacting components in the asphalt. This test method has been applied to recycled blends. Results from these tests have clearly shown differences in different combinations of asphaltic materials.

Concerning determination of the required quantity of modifier to rejuvenate an aged binder, the current technology employs a blend chart as shown in Figure 1 (Reference 25). The percent of modifier required depends on the grade of available modifier and intrinsically should depend on the chemistry of the two materials to be blended. Chevron (Reference 25) identifies the following as desirable properties of a modifier suitable for hot-mix recycling:

- Ease of dispersion,
- High flashpoint,
- Low volatile loss during hot mixing,
- Resistance to hardening, and
- Uniformity.

However, the biggest problem is the selection of a specific modifier from a group of modifiers. Some current suggestions (Reference 26) indicate that the following factors need to be assessed:

- The type of performance problem to be cured,
- Cost-effectiveness,
- Environmental effects,
- Construction and performance effectiveness,
- Energy effectiveness,
- Availability, and
- Recyclability.

The results presented within this report constitute work performed in a laboratory in which physical and chemical tests were performed on field-aged

It is argued that if the modifier is aiding in resolubilizing the asphaltenes, then the value of Equation(1) will be positive; otherwise a negative value will indicate that the modifier is destabilizing the asphalt. Dunning et al. (Reference 6) postulated that a modifier of suitable asphaltene dispersive ability should have 9 percent minimum polar compound content and 60 percent minimum aromatic compound content, as determined by the Clay-Gel (ASTM D2007) method. Anderson et al. (Reference 13) observed that high paraffin content (which corresponds to a high saturate content using Clay-Gel analyses) promoted premature cracking in pavements which is a performance indicator of composition incompatibility. Rostler et al. (References 18 and 19) developed the original compatibility parameter which they defined to be the ratio of nitrogen bases (N) to paraffins (P). These two chemical fractions are determined by the Rostler-Sternberg chemical precipitation method (formerly ASTM D-2006). This compatibility parameter (N/P) was developed for fresh binders. A value of N/P greater than 0.5 is considered (Reference 6 and personal communication from V. Puzinauskas) to represent a compatible system. Davidson et al. (Reference 5) and Canessa (Reference 20) report that the use of modifiers with N/P greater than 0.50 would yield durable pavements. Durability is measured by the Rostler (References 18 and 19) durability parameter which will be defined later.

The whole subject of compatibility rests on the ease with which the asphaltenes are dispersed. An asphalt that will remain durable for a long period of time will be compatable system where all components remain dispersed with little or no precipitation of asphaltenes. That means that the maltenes will be able to keep the asphaltenes dispersed. If the asphaltene percentage becomes too large due to oxidation or the maltenes lose their ability to keep the asphaltenes in solution, then the whole system breaks down. The pavement then becomes brittle and/or failure occurs. The question of compatibility is important in recycling. By adding a modifier to an aged pavement one goal is to obtain a system that will redisperse the asphaltenes. If the modifier added cannot help redisperse the asphaltenes, then compatibility becomes a problem. Altgelt et al. (Reference 21) describe the colloidal effects of asphaltenes on viscosity. Petersen (References 22 and 23) stresses the significance of compatibility to durability or performance characteristics of pavements. He argues that a knowledge of the compatibility of interacting components in asphalt can lead to durable paving materials by allowing better investigated the effects of modifiers on properties of aged binders with emphasis on physical and performance properties. Davidson et al. (Reference 5), Dunning et al. (Reference 6), Kari et al. (Reference 7), Santucci et al. (Reference 8), Kennedy et al. (Reference 9) and Escobar et al. (Reference 10) have all conducted research work in the area of asphalt recycling. The National Cooperative Highway Research Program (NCHRP) Synthesis 54 (Reference 11), presented the first comprehensive summary of recycling information resulting from the NCHRP Study 1-17. The work in this report which was co-sponsored by the Federal Highway Administration includes Project No. 39, Recycling Asphalt Pavements (Reference 12); FHWA-TS-79-204 by Anderson et al. (Reference 13), Evaluation of Selected Agents in Flexible Pavement Recycling; Implementation Package 75-5 which includes Office of Research Studies on "Softening or Rejuvenating Agents for Recycled Bituminous Binders," "Tests for Efficiency of Mixing Recycling Asphat Pavements," "Data Bank for Recycled Bituminous Concrete Pavement," and "Materials Characterization of Recycled Bituminous Paving Mixtures" (Reference 14). The Corps of Engineers (References 15 and 16) and the Navy (Reference 17) have sponsored work in recycling as applied to Army, Air Force and Navy flexible pavements. The Asphalt Institute has also been conducting research in recycling.*

In the engineering of recycling, the quantitative treatment of the subject of material compatibility has been sparse. Physical properties are the norm in all cases involving modifier-aged asphalt applications. That is, as long as the modifier softens the aged binder to a desired consistency and meets other physical and performance tests, the blend is considered acceptable. However, the modifier and the aged asphalt which constitute the binder could be incompatible on a chemical basis. Dunning et al. (Reference 6) reported that compatibility of a modifier with aged asphalt could be established by evaluating the slope of the relationship between log-log viscosity (centistokes) against log (559.7 - percent modifier). These authors proposed that if the modifier should cause a drastic drop in viscosity, then the compatibility evaluation could be judged by satisfying the following expression:

$$\frac{d^2 \text{ log-log Viscosity}}{d \log (559.7 - \text{percent modifier})^2} > 0 \qquad (1)$$

where d = derivative and viscosity is in centistokes

*Personal communication from V. Puzinauskas.

SECTION II
LITERATURE REVIEW

STATUS OF RECYCLING TECHNOLOGY

The concept of recycling asphalt pavements has been utilized in the paving industry in the United States since the 1920s. The American Society for Testing and Materials (ASTM) is trying to develop a recycling agent specification. The West Coast User-Producer Group has already adopted a recycling agent specification and several states have developed their own permissive specifications. The National Cooperative Highway Research Program (NCHRP), in Report No. 224 has established guide specifications for use in recycling projects. However, problems still exist in defining what physical and chemical properties a modifier should possess for compatibility with an aged binder. Many products are marketed today for use as modifiers in recycling old pavements. They include soft asphalts, highly paraffinic oils and highly aromatic oils. In many cases almost all available modifiers comply with current specifications, but do not adequately ensure compatibility and performance. This research project was initiated to determine chemical and physical tests and correlations between the two, so that a standard laboratory could select appropriate modifiers for use in specific recycling projects.

The technology of recycling began about 1931 in Singapore and reappeared in 1948 in India. Newcomb and Epps, (Reference 1) summarize the growth of recycling technology from 1931 to 1980 and report case histories in which recycling was cost-effective. They also list the advantages of reusing asphalt concrete materials as follows: (1) stabilize the cost of pavement construction, (2) conserve petroleum and aggregate resources, (3) reduce the amount of energy required to maintain and rehabilitate pavements, (4) preserve the environment, and (5) preserve existing pavement geometrics. Epps et al. (Reference 2) report that recycling can be accomplished either in place or in a central plant and can be either a hot or cold process. The process of recycling almost always requires the use of some petroleum product to restore the aged asphalt binder to an acceptable level of consistency. These petroleum extracts are soft asphalts, high polar content oils or high aromatic oils, all of which will be referred to in this publication as modifiers. Carpenter et al. (Reference 3) and Holmgreen et al. (Reference 4)

Step 4--Additive and Binder Study. Combinations of each of three of the four aged asphalt binders and each additive were blended and characterized chemically and physically. Optimum additive proportions for recycling the mixtures were determined by viscosity. The fourth aged binder will be a subject of ongoing work not included in this report.

Step 5--Recycled Mixture Characterization. Additive proportions determined in Step 4 were used to design laboratory recycled mixtures using the Marshall method. They were then subjected to accelerated aging. Physical testing of these mixtures was performed at time periods of 1 week, 1 month, 3 months, and 6 months. Chemical testing was reaccomplished at the end of the aging period. A tentative guide specification for recycling agents to be used in hot central plant processes was developed, based on information obtained during this research effort.

Phase II consists of research on additional aged asphalts and modifiers to refine the tentative guide specification using the physical and chemical tests that most reliably predict asphalt/additive compatibility. Also, a test plan is being developed to construct, monitor, and report field test section performance. These field trials will validate the new guide specification.

Step 1 of this research effort involved a review of previous work in recycling which included visits and contacts with experts who were familiar with physical and chemical testing procedures of interest. These included: American Society for Testing and Materials, Ashland Oil Company, The Asphalt Institute, Chevron Research Company, Douglas Oil Company, Federal Highway Administration and its affiliates, Matrecon, Inc., Mobile Oil Company, Montana State University, Pennsylvania State University, Petroleum Sciences, Inc., Shell Oil Company, Texas A & M University, University of Washington, Waterways Experiment Station, Western Research Institute (formerly Laramie Energy Technology Center), and Witco Chemical Corporation.

Section II will summarize the literature concerning recycling technology and methods of characterization of asphaltic materials.

OBJECTIVE

The objective of this effort was to formulate a procedure by which a standard laboratory can define appropriate modifiers for recycling old paving-grade asphalts in hot central plants.

SCOPE

This research effort was intended to investigate the physical and chemical changes occurring to aged-asphalt concrete in the presence of modifiers in hot central plant-recycling operations. Review of past work in this area was conducted to develop laboratory and field-testing programs. A hypothesis concerning compatibility and changes during recycling based on existing technology and this research was prepared and tested. Physical and chemical tests were performed at the laboratory scale to define, test, and extend the hypothesis. Consultants from the asphalt technology field were employed to take full advantage of available knowledge.

CONDUCT OF RESEARCH

This research was composed of two phases. Phase I included the literature review and the laboratory study. The following five steps were included in Phase I:

Step 1--Pavement Identifications and Sample Collection. Aged pavement cores from four Air Force Bases were obtained. Base locations were climatically different and their pavements exhibited various degrees and causes of distress. The installations from which pavement samples were taken were Pope AFB NC, Loring AFB ME, Holloman AFB NM, and Ellsworth AFB SD.

Step 2--Characterization of Mixture and Binder. The aged binders were extracted and recovered from the mixture. A series of physical and chemical tests were performed to establish the baseline data needed to observe changes after simulated hot central plant recycling.

Step 3--Additive Evaluation. A number of asphalt additives from different manufacturers were obtained and characterized chemically and physically. Additives representing a wide spectrum of chemical and physical characteristics were selected for use in the blend study.

1. Add usable information to the available generic fraction and physical data,
2. Provide solution property information and hence some measure of compatibility,
3. Provide information that lends itself to some data base or recorded application,
4. Be adaptable to the available equipment,
5. Be adaptable to the analysis of recycling agents and blends,
6. Involve the use of relatively safe reagents,
7. Minimize cost without reducing accuracy,
8. Provide supportive information (examples are EPR and NMR), and
9. Be supported by expert opinion.

Based on the critical listing above, the following methods were chosen:

1. Clay-Gel Compositional Analyses (with modifications*)
2. Heithaus Flocculation Ratio
3. High-Pressure Gel Permeation Chromatography
4. Elemental Analysis
5. Infrared and Nuclear Magnetic Resonance (limited)
6. Electron Paramagnetic Resonance

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*The Clay-Gel compositional analyses technique was modified for use in this research effort to make it applicable to a variety of aged asphalts, modifiers and blends. Details of the method and modifications can be found in Appendix A.

SECTION III
MATERIALS AND TESTING

MATERIALS

The materials used in this research effort consisted of three aged airfield pavements and over 30 modifiers obtained from a variety of manufacturers. The aged pavements were the same pavements used in the "Asphalt Fatigue" project (Reference 77) performed at the New Mexico Engineering Research Institute.

The three aged pavements were obtained from Pope Air Force Base, North Carolina; Loring Air Force Base, Maine; and Holloman Air Force Base, New Mexico. These cores were from hot-wet, cold-wet, and hot-dry climatic regions, respectively. The following paragraphs briefly present the physical condition of the aged pavements before cores were taken.

The Pope Air Force Base samples were taken from a taxiway constructed in 1942 and 1943. The taxiway is 1,500 feet long and 150 feet wide, and is used as an access to the "hot cargo" area between Taxiways 6 and 7 and as a runup area for aircraft formations (Reference 77). Traffic was composed primarily of C-47, C-119, C-123, C-130 and C-141 military transport aircraft. This pavement was severely fatigued and was composed of excessive amounts of fine aggregate material.

The pavement samples from Loring Air Force Base were obtained from a taxiway constructed in 1951 and 1952, with a subsequent overlay in 1960. Only the bottom layers below the overlay were used in this study. The traffic was mostly B-52 and KC-135 aircraft. This pavement was so brittle that it fractured into small pieces when a percussion hammer was used to cut slabs. This pavement was also fatigued.

Holloman Air Force Base samples were removed from a main taxiway 75 feet wide and 1,150 feet long. The traffic on this section consisted almost entirely of T-38 aircraft. The taxiway was constructed between 1942 and 1943 with overlays in 1963 and 1970. Very little fatigue was observed on this taxiway, with only two areas showing alligator cracking.

At the time of this report, testing has been completed on recycled blends at Pope, Loring, and Holloman AFBs. In addition, Pope AFB mixtures have completed their 178-day accelerated aging and all chemical and physical testing of the mixtures and the extracted binder has been completed. Also, Loring AFB mixtures have undergone their 125-day accelerated aging and all physical and chemical testing of these mixes and extracted binders are complete.

At the beginning of this effort, over 30 modifiers were obtained from a variety of manufacturers. These included soft asphalts, highly paraffinic oils and highly aromatic recycling agents. After the initial clay-gel analyses were performed, this number was reduced to 14 modifiers that satisfied the criteria set forth in the testing plan (see Section IV). Table 1 lists the Clay-Gel data for the 14 modifiers used in the laboratory testing scheme.

TESTING

The testing program involved the application of physical and chemical methods to characterize aged binders, modifiers, blends, RTFO aged blends and recycled Marshall mixtures.

Physical Characterization

Aged Binders

Field-aged binders were recovered from cores for pavements from Pope, Loring, and Holloman AFBs as described by Lenke (Reference 77). The recovery process was modified in this study by applying a Buchi rotovap system to preclude traces of recovery solvents. A continuous purge of nitrogen was maintained during the evaporation to minimize the oxidation potential. The recovered binders were characterized according to the following methods:

1. Viscosity (ASTM D-2170 and D-2171) at 140°F and 275°F,
2. Penetration (ASTM D-5) at 39.2°F and 77°F,
3. Ductility (ASTM D-113) at 77°F and 60°F,

TABLE 1. CLAY-GEL DATA FOR MODIFIERS

Modifier identification	Asphaltenes	Saturates	Aromatics	Polars	P/S
MBD-1	0.25	84.34	12.68	2.74	0.03
MBD-2	20.35	20.78	23.19	35.48	1.72
MBD-2B	21.82	17.71	24.90	35.07	1.98
MBD-3	9.78	15.96	24.34	49.87	3.12
MBD-3B	0.62	21.59	24.22	53.57	2.18
MBD-4	0.73	50.49	43.95	4.97	0.10
MBD-5	0.20	23.46	49.02	27.73	1.18
MBD-6A	23.79	15.22	26.37	34.63	2.28
MBD-6B	8.51	21.57	26.96	43.13	2.00
MBD-7A	0.24	22.17	62.40	15.55	0.70
MBD-7C	0.47	24.94	56.90	17.69	0.71
MBD-8A	0.30	17.78	60.20	21.98	1.24
MBD-8C	0.18	15.87	65.18	18.77	1.18
MBD-9	0.12	6.44	64.50	29.07	4.51

4. Low-temperature viscosities at 39.2°F and 77°F, using the Schweyer Rheometer (Reference 78), and

5. Rolling Thin-Film Oven condition (ASTM D-2872).

All of these test methods can be found in Volume 04.03 of the 1983 Annual Book of ASTM Standards (Reference 79), except the Schweyer Rheometer Procedure (Reference 78).

The recovered property data of the aged binders as evaluated in this recycling study is summarized in Table 2.

Modifiers

The modifiers were evaluated for flash point and viscosity. Flash point test (ASTM D-92) was performed to ensure safety of the personnel and equipment in the laboratory. Viscosity evaluation was done at 100, 140, and 212°F so that temperature susceptibilities could be investigated. The viscosity data at 140°F were useful in calculating the proportions of modifiers required in design of aged asphalt-modifier blends. The blends were designed by the aid of the blend chart shown in Figure 1.

All modifiers used in the testing program were evaluated for weight loss (ASTM D-2872) after a strong recommendation by ASTM Subcommittee D04.37 (Reference 80).

Tests on Blends

The viscosities (centi-Stokes) of aged binders and modifiers at 140°F, were used to determine modifier requirements,as described above. The resulting blends were evaluated for viscosity at 140°F and compared with target viscosities of 4000 poises (P), 500 P and 2000 P for Pope, Loring and Holloman AFBs materials, respectively. These target values were determined after consulting with local authorities in the areas where these bases are located with reference to the grade of asphalt used in the respective construction operations. Once the target viscosities were met within the AC-40, AC-5 and AC-20 ASTM limits (Reference 79, ASTM D-3381), then each blend was evaluated using the full range of tests which were listed in the section on aged binders.

TABLE 2. RECOVERED ASPHALT PROPERTIES

Property	Pope AFB Asphalt	Loring AFB Asphalt	Holloman AFB Asphalt
Penetration at 39.2°F, 200g, 60 s, 0.1 mm	11	13	2
Penetration at 77°F, 100g, 5 s, 0.1 mm	22	33	6
Viscosity at 39.2°F, 0.056 s^{-1}, P	1.20E09	2.33E08	2.03E09
Shear Susceptibility "c" at 39.2°F	0.71	0.99	0.63
Viscosity at 77°F, 0.05 s^{-1}, P	2.40E07	8.78E05	1.15E07
Shear Susceptibility "c" at 77°F	0.61	0.83	0.71
Viscosity at 140°F, P	56,800	6,375	172,795
Viscosity at 275°F, cSt	1,413	554	1,967
<u>Clay-Gel Composition</u>			
Asphaltenes, %	43.57	27.61	35.94
Saturates, %	10.79	15.74	11.63
Aromatics, %	12.78	14.30	10.56
Polars, %	32.82	42.33	41.88
Polars/Saturates (P/S)	3.04	2.69	3.60
Asphaltenes + Saturates (A + S)	54.36	43.35	47.57

The procedure for preparation of the blends, the timing between the preparation and the testing, and the sequence of tests run was kept constant for all blends and throughout all test matrices. This was followed to keep the variables at a minimum. The amount of heating, cooling, freezing and reheating was kept constant and at a minimum.

The penetration-temperature data were used to develop and evaluate the following relationship:

$$TPI = \frac{\text{Pen at } 77°F}{\text{Pen at } 39.2°F} \tag{7}$$

where TPI = temperature penetration index. The TPI is considered (Reference 81) to denote the temperature susceptibility of the material at a pair of temperatures.

The low-temperature viscosity data obtained by the Schweyer constant pressure rheometer can be used to compute viscosities over a range of shear rates. Thus, shear susceptibilities can also be determined at the same range of shear rates. The data to be discussed later will pertain to a shear rate of 0.05 sec^{-1} which will include viscosities and shear susceptibility parameters. The shear susceptibility is usually designated by "c". A value of "c" less than one indicates that the materials evaluated are pseudoplastic. A "c" value equal to unity indicates Newtonian behavior, while "c" values greater than unity are indicative of dilatant behavior.

High-temperature behavior of the blends was evaluated at 140°F and 275°F. All blends evaluated at 140°F satisfied the target blend viscosity levels. Thus, the viscosities at 275°F were considered to be the best candidates for evaluating the differences in high-temperature behavior of the materials tested.

The rolling thin-film oven (RTFO) samples were evaluated for viscosity at 140°F, penetration at 39.2°F and 77°F, and ductility at either 77°F or 60°F. The lower-temperature ductility was chosen for Loring and Holloman AFBs blends. The RTFO penetration values were expressed as percentages of unaged penetration values. The aged viscosity data was used to calculate the aging index, which is defined by the following expression:

$$\text{Aging Index (AI)} = \frac{\text{Viscosity at 140°F after RTFO}}{\text{Viscosity at 140°F before RTFO}} \qquad (8)$$

Tests on Recycled Mixes

Recycled mixes were made for Pope AFB and Loring AFB materials. The compacted Marshall mixtures were evaluated for the following properties:

1. Bulk specific gravity (ASTM D-2726),
2. Rice specific gravity (ASTM D-2041),
3. Resilient modulus (Schmidt--Reference 82) and ASTM D-4123 (Reference 79) at 77° ± 5°F, and
4. Water susceptibility--Specimens were vacuum-soaked for 1 hour under 21 inches of Mercury. They were left in water with no vacuum for another hour and each was evaluated, using the resilient modulus device at 77°F.

Some of the compacted cores were placed in an oven at 140°F to induce accelerated aging conditions. These aging samples were evaluated,using the resilient modulus device at the end of 7-, 30-, 89- and 178-day periods for Pope AFB mixes, and 7-, 28-, 90-, 110- and 125-day periods for Loring AFB mixes. The Holloman AFB mixes have not been prepared at the time of this report

Two controls were prepared for each test matrix. These were manufactured with parent-recovered aggregates, a local source aggregate, and fresh AC-40 and AC-5 asphalts, respectively.

The data for the recycled mixes will be presented and discussed in Section V. The next subsection will describe the test methods used in the chemical characterization phase of the testing program.

Chemical Characterization

This phase of characterization involved the use of the following methods:

1. Clay-Gel (ASTM D-2007),
2. Compatibility test,
3. High-Pressure Gel Permeation Chromatography (HP-GPC),
4. Elemental Analysis,
5. Infrared Spectroscopy (IR),
6. Nuclear Magnetic Resonance (NMR), and
7. Electron Paramagnetic Resonance (EPR).

Compositional Analyses

The Clay-Gel procedure (ASTM D-2007-75) was used in this research effort. Modifications were implemented to make the technique applicable to a variety of asphaltic materials. A detailed description of the original ASTM Clay-Gel procedure and the modifications can be found in Appendix A.

Compatibility Tests

The Heithaus (Reference 48) and Waxman, et al. (Reference 51) concepts were incorporated in evaluating the peptizability characteristics of aged asphalts and modifiers. Compatibility was then inferred from the test results.

Five 1-gram samples were tested for each material by using a polar solvent (toluene) and a titrant solvent (n-dodecane). The amount of titrant solvent required to induce precipitation of the asphaltenes was noted for a particular solution of binder-toluene. Precipitation was observed under a microscope at 100-150X. The information on volumes of solvents and amounts of material was used to calculate the following solution properties:

1. Asphaltene peptizability (P_a-Heithaus),
2. Maltene peptizing power (P_0-Heithaus),
3. State of peptization of the asphaltene dispersion (P - Heithaus), and
4. The angular measure of solvent characteristics (cot ϕ-Waxman, et al.)

The detailed description of the test method, a photograph of equipment setup and a flocculated specimen (Figure B-1), and the mathematical relationship between the solution property parameters are included in Appendix B.

High-Pressure Gel Permeation Chromatography

High-Pressure Gel Permeation Chromatography (HP-GPC) is a separation process based on molecular size. Dr. P. W. Jennings of Montana State University is involved in an extensive 17-state project using HP-GPC to characterize a variety of pavements. Samples from this research effort were sent to Dr. Jennings for analysis. The samples included aged pavements, modifiers, blends and Rolling Thin-Film Oven (RTFO) aged blends.

Elemental Analysis

The percent carbon, hydrogen and nitrogen were determined by elemental analyses on all the unaged and aged blends. This technique involves the decomposition of an organic material from which the percentages of carbon, hydrogen and nitrogen are determined by the amount of carbon dioxide (CO_2), water (H_2O) and ammonia (NH_3) formed.

Electron Paramagnetic Resonance

Electron Paramagnetic Resonance (EPR) was investigated as a possible technique for evaluating recycling agents, asphalts and blends. EPR is a spectroscopic technique that irradiates a sample with microwave radiation which excites unpaired electrons. For every 1,000 electrons in the low-energy state, 998 are in the high-energy level. Although the two levels are almost equal in population, the absorption of energy in the lower state exceeds emission from the upper level because of the Boltzmann population distribution equation:

$$\frac{n \text{ upper}}{n \text{ lower}} = e^{-\Delta E/kT}$$

where k is the Boltzmann's constant (1.38×10^{-16} erg $°K^{-1}$) and T is the absolute temperature (°K). Consequently, there will be a net absorption of energy, which results in a signal on a spectrum.

Unpaired electrons are not always found in materials, but when a sample has unpaired electrons, these electrons are highly reactive and subject to oxidation. Therefore, some preliminary work was performed to determine if asphalts had an EPR signal. It was found that asphalts indeed do have an EPR signal, but after reviewing several papers involving EPR work on other petroleum products, the magnitude of a comprehensive study was realized. Therefore a separate project was initiated by the US Air Force.

Infrared Spectroscopy

Infrared Spectroscopy (IR) experiments were conducted on Pope, Loring and Holloman AFBs control samples as well as unaged blends. These samples were analyzed at the Western Research Institute in Laramie. The samples were analyzed using a method developed for asphalts by Claine Petersen (References 65 and 66) which employs the use of differential IR. From the analysis of the differential IR spectra one can obtain the concentrations of ketones, free caboxylic acids, salts of carboxylic acids, sulfoxides, and saponifiable components (mainly anhydrides). The above compounds represent oxidation products of carbon and sulfur-containing compounds in asphalts, and will be affected by the asphalt's aging.

Nuclear Magnetic Resonance

The Nuclear Magnetic Resonance (NMR) center at Colorado State University has been contacted regarding the running of NMR experiments on solid asphalt samples. This method will be used to determine the ratio of polar to aromatic components in the asphalt samples. This ratio can then be used to substantiate the data obtained from the Clay-Gel separation.

SECTION IV

TEST PLAN FOR LABORATORY INVESTIGATION

A laboratory investigation was planned to include as many modifiers and aged asphalts as the budget and project time could permit. The practical constraint was the procurement of a good number and wide variety of modifiers. From the Clay-Gel composition analyses of the modifiers, two chemical parameters were identified for use in this study. These parameters are the polar/saturate (P/S) ratio and the percent generic aromatic content. These chemical parameters were chosen with the assumption that variation of the P/S ratio and the percent generic aromatic content would furnish information on compatibility, solvency characteristics and such performance parameters as ductility. Flash point information was used to check the volatility of the candidate products.

The identification of the above chemical parameters enabled the researchers to design test matrices. These matrices, 3 by 3, were designed for each aged asphalt material to be studied. The two parameters P/S and percent generic aromatic content were assigned low, medium, and high values and/or ranges on an arbitrary basis. The values and/or ranges were obtained from Clay-Gel composition analyses consisting of more than 30 modifiers obtained from various producers. The P/S parameter was set at less than 1.0 for low, from 1.0 to 2.0 for medium, and greater than 2.0 for the high category. The percent generic aromatic content was set at less than 25 percent for low, from 25 to 50 percent for medium, and greater than 50 percent for the high category.

POPE AFB TEST MATRIX

The test matrix consisted of asphalt from Pope AFB as the parent aged binder and nine modifiers which included highly paraffinic, soft asphalts and highly aromatic products as shown in Figure 2. The Polar/Saturate ratio increases from left to right while the percent aromatic content increased from top to bottom. The choice of the ranges of values indicated on the figure was made, based on the samples of modifiers available to the research team. Thus, the ranges were set to cover the spectrum of products which were obtained.

PERCENT AROMATIC \ POLAR/SATURATE	LOW	MED	HIGH	
LOW	MBD-1[a]	MBD-2[b]	MBD-3	< 25%
MEDIUM	MBD-4[a]	MBD-5	MBD-6A[b]	> 25% < 50%
HIGH	MBD-7A	MBD-8A	MBD-9	> 50%
	< 1.0	> 1.0 < 2.0	> 2.0	

[a]High Paraffinic Oils

[b]Soft Asphalts

Figure 2. Pope AFB Test Matrix.

TABLE 8. PHYSICAL PROPERTIES OF BLENDS AFTER RTFO (LORING AFB)

Blend identi-fication	Pen at 39.2°F, 200 g, 60 s		Pen at 77°C, 100 g, 5 s		Viscosity at 140°F		Ductility 5 cm/min, cm	
	0.1 mm	Unaged, %	0.1 mm	Unaged, %	P	Aging index	77°F	60°F
MBD-12	42	67	90	62	1350	3.1	100+	
MBD-2B2	19	45	77	56	1138	2.6	100+	100+
MBD-3B2	35	64	89	52	986	1.8	100+	100+
MBD-42	25	56	58	43	3060	6.2	100+	64
MBD-52	33	60	97	53	962	2.2	100+	100+
MBD-6B2	32	58	109	66	871	1.8	100+	100+
MBD-7A2	35	76	111	65	788	1.7	100+	100+
MBD-8A2	41	77	134	79	748	1.6	100+	100+
MBD-92	34	71	111	71	786	1.5	100+	100+
Control	6	46	28	85	9665	1.5	100+	7
ASTM D-3381 AC-5, Table 1	NS	NS	NS	NS	2500 max	NS	100 min.	
ASTM D-3381 AC-5, Table 2	NS	NS	NS	NS	2500 max	NS	100 min.	

NOTES: Pen = Penetration
P = Poises
NS = Not specified by ASTM
Control refers to the aged binder recovered from RAP.

TABLE 7. PHYSICAL PROPERTIES OF BLENDS AFTER RTFO (POPE AFB)

Blend identification	Pen at 39.2°F, 200 g, 60 s		Pen at 77°C, 100 g, 5 s		Viscosity at 140°F		Ductility 77°F
	0.1 mm	Unaged, %	0.1 mm	Unaged, %	P	Aging index	5 cm/min, cm
MBD-11	19	38	28	40	118,700	29.9	4
MBD-21	17	48	37	57	23,620	7.1	10
MBD-31	14	74	33	57	10,220	2.9	100+
MBD-41	5	14	15	24	222,000	63.4	4
MBD-51	8	22	20	29	57,470	14.4	8
MBD-6A1	20	59	38	52	13,520	4.0	100+
MBD-7A1	9	24	21	31	43,020	13.2	9
MBD-8A1	21	58	39	53	14,040	3.7	59
MBD-91	18	50	37	51	12,420	3.5	100+
Control	3	27	8	36	534,000	9.4	4

NOTES: Pen = Penetration
P = Poises
Control refers to the aged binder recovered from RAP.

This distribution of effects was not totally duplicated from one test matrix to another. Such was not an anomaly because the three aged asphalts are different and probably came from different crude sources.

The negative effect in Figures 5, 6, and 7 refers to a blend whose viscosity was higher than the target value and outside the guide tolerance in Table 1 of ASTM D-3381. This result further implied that more modifier was required to meet the target viscosity or a lower viscosity modifier would be required. The zero effect meant that the blend viscosity was on target or within the guide ASTM limits. The positive effect meant that blend viscosity was lower than target viscosity. It further meant that the blend viscosity was outside the lower ASTM limit and hence the modifier content needed to be reduced.

Tables 7, 8, and 9 list RTFO properties of the blends for all matrices. In all tables modifiers MBD-1 and MBD-4 yielded the highest aging indices in the blends and correspondingly the lowest ductilities at 77°F for the Pope AFB blends, at 60°F for the Loring AFB and Holloman AFB blends. Other modifiers, such as MBD-5 and MBD-7A, led to the next higher aging indices for the Pope AFB blends, MBD-2B and MBD-5 for the Loring AFB blends and MBD-3, MBD-6A, and MBD-2 for the Holloman AFB blends. Some modifiers produced blends of higher aging indices than the indices of the aged binders (controls). This same phenomenon is evident in the results of a recent study (Reference 83) in which two fresh AC-20 asphalts were modified for a target viscosity of 1000 Poises at 140°F. Three modifiers were used in the study of reference. This phenomenon is probably caused by the variation in the concentration of lighter ends in the different modifiers. These results indicate to the NMERI research personnel that other aspects of the asphalt-modifier relationship need to be investigated in order to assess the overall improvement and/or susceptibility to damage. This is why asphalt-modifier compatibility studies are an essential element in recycling operations.

Recycled Mixtures

Recycled Marshall mixtures were manufactured for binder contents of 6 percent for the Pope AFB matrix and 5.5 percent of the Loring AFB matrix. Two control samples were prepared for each matrix. The nomenclature for the

Legend

- \- Negative Effect
- \+ Positive Effect
- 0 No Effect (target viscosity met)

- MBD-1	- MBD-2	+ MBD-3
NO SUITABLE MODIFIER SELECTED	+ MBD-5	+ MBD-6A
- MBD-7A	+ MBD-8A	+ MBD-9

Figure 7. Effects of Modifiers on Blend Viscosities (Holloman AFB).

Legend

- \- Negative Effect
- \+ Positive Effect
- 0 No Effect (target viscosity met)

- MBD-1	+ MBD-2B	0 MBD-3B
+ MBD-4	0 MBD-5	0 MBD-6B
0 MBD-7A	0 MBD-8A	- MBD-9

Figure 6. Effects of Modifiers On Blend Viscosities (Loring AFB).

Legend

- \- Negative Effect
- \+ Positive effect
- 0 No effect (target viscosity met)

- MBD-1	- MBD-2	+ MBD-3
- MBD-4	+ MBD-5	0 MBD-6A
+ MBD-7A	0 MBD-8A	+ MBD-9

Figure 5. Effects of Modifiers on Blend Viscosities (Pope AFB).

TABLE 6. PHYSICAL PROPERTIES OF UNAGED BLENDS (HOLLOMAN AFB)

Blend	Modifier, %	Pen at 39.2°F, 200 g, 60 s, 0.1 mm	Pen at 77°F, 100 g, 5 s, 0.1 mm	η at 39.2°F, 0.05 s^{-1} x 10^7 P	"C" at 39.2°F	η at 77°F, 0.05 s^{-1} x 10^6 P	"C" at 77°F	η at 140°F, P	η at 275°F, cSt	Ductility at 77°F, 5 cm/min, cm
MBD-13	17.2	38	66	0.61	0.480	3.74	0.614	1790	302	10
MBD-23	75.5	27	70	1.67	0.619	3.19	0.658	1806	369	22
MBD-33	63	20	63	5.65	0.862	1.74	0.824	1785	196	100+
	a---	a---	a---	a---	a---	a---	a---	a---	a---	a---
MBD-53	22.5	29	77	5.57	0.716	2.23	0.739	1952	292	100+
MBD-6A3	57	28	86	5.65	0.862	2.14	0.838	1853	380	100+
MBD-7C3	20	32	78	1.46	0.667	1.58	1.030	2125	295	100+
MBD-8C3	19	26	62	2.10	0.721	2.74	0.735	1990	304	96
MBD-93	20	23	78	8.78	0.805	2.11	0.844	2139	294	100+
Control	0	2	6	202.80	0.628	114.75	0.711	172,795	1967	2.5
ASTM D-3381 for AC-20, Tab. 1	NS	NS	40	NS	NS	NS	NS	2000±400	210	20 min (77°F)
ASTM D-3381 for AC-20, Tab. 2	NS	NS	60	NS	NS	NS	NS	2000±400	300	50 min (77°F)

[a]No suitable modifier at hand to fit in matrix.

NOTES: Pen = Penetration
η = Viscosity
P = Poises
NS = Not specified by ASTM
Control refers to the aged binder recovered from RAP.

TABLE 5. PHYSICAL PROPERTIES OF UNAGED BLENDS (LORING AFB)

Blend	Modifier, %	Pen at 39.2°F, 200 g, 60 s, 0.1 mm	Pen at 77°F, 100 g, 5 s, 0.1 mm	η at 39.2°F, 0.05 s^{-1} x 10^7 P	"C" at 39.2°F	η at 77°F, 0.05 s^{-1} x 10^6 P	"C" at 77°F	η at 140°F, P	η at 275°F, cSt	Ductility at 77°F, 5 cm/min, cm
MBD-12	12.5	63	145	2.62	0.684	5.39	0.787	436	190	100+
MBD-2B2	81.5	42	137	4.23	0.772	5.73	0.770	441	183	100+
MBD-3B2	41	55	170	3.65	0.720	2.80	0.877	544	189	100+
MBD-42	9	45	134	5.50	0.849	5.91	0.836	496	211	100+
MBD-52	19.5	56	183	3.45	0.826	3.09	0.834	435	157	100+
MBD-6B2	45	55	166	4.61	0.875	4.22	0.854	479	166	100+
MBD-7A2	17	46	171	5.61	0.888	5.61	0.678	458	169	100+
MBD-8A2	18.5	53	170	3.42	0.798	3.87	0.745	456	175	100+
MBD-92	18	48	157	4.04	0.924	4.14	0.829	519	165	100+
Control	0	13	33	233	0.991	87.8	0.828	6375	554	11.2
ASTM D-3381 for AC-5, Tab. 1	NS	NS	120 min	NS	NS	NS	NS	500±100	110 min	100 min
ASTM D-3381 for AC-5, Tab. 2	NS	NS	140 min	NS	NS	NS	NS	500±100	175 min	100 min

NOTES: Pen = Penetration
η = Viscosity
P = Poises
NS = Not specified by ASTM
Control refers to the aged binder recovered from RAP.

TABLE 4. PHYSICAL PROPERTIES OF UNAGED BLENDS (POPE AFB)

Blend	Modifier, %	Pen at 39.2°F, 200 g, 60 s, 0.1 mm	Pen at 77°F, 100 g, 5 s, 0.1 mm	η at 39.2°F, 0.05 s^{-1} x 10^7 P	"C" at 39.2°F	η at 77°F, 0.05 s^{-1} x 10^6 P	"C" at 77°F	η at 140°F, P	η at 275°F, cSt	Ductility at 77°F, 5 cm/min, cm
MBD-1	16	50	70	3.3	0.43	3.3	0.53	3,970	277	34
MBD-2	65	35	65	11	0.62	3.6	0.53	3,340	414	98
MBD-3	36	19	58	68	0.96	3.7	0.86	3,470	426	100+
MBD-4	10	37	63	5.8	0.52	3.0	0.64	3,500	350	100+
MBD-5	13	37	68	13	0.66	3.2	0.73	3,990	405	100+
MBD-6A	43	34	73	8.9	0.65	2.3	0.76	3,420	497	100+
MBD-7A	13	37	71	10	0.68	2.7	0.72	3,260	350	100+
MBD-8A	16	36	68	13	0.68	2.6	0.75	3,760	405	100+
MBD-9	12	36	74	16	0.79	2.4	0.80	3,500	424	100+
Control	0	11	22	120	0.71	24	0.61	56,800	1,413	9

NOTES: Pen = Penetration

η = Viscosity

P = Poises

Control refers to the aged binder recovered from the Recovered Age Pavement (RAP).

TABLE 3. PHYSICAL PROPERTIES OF MODIFIERS

Modifier designation	Viscosity at 100°F, P	Viscosity at 140°F, P	Viscosity at 212°F, P	Flash point, COC, °F	Weight loss, %
MBD-1	.77	.25	.07	420	2.49
MBD-2	15,300.00	490.00	14.00	555	.40
MBD-3	20,000.00	540.00	9.70	535	.34
MBD-4	.19	.08	.03	325	29.08
MBD-5	16.00	2.80	.25	435	2.55
MBD-6A	5,400.00	300.00	9.80	460	1.79
MBD-7A	6.20	1.00	.15	445	1.32
MBD-8A	9.90	1.80	.24	480	.40
MBD-9	27.00	2.30	.19	420	2.71
MBD-2B	9,670.00	324.00	8.30	500	.74
MBD-3B	670.00	58.00	3.60	600	ND[a]
MBD-6B	1,676.00	90.00	3.20	515	.10
MBD-7C	5.81	1.10	.16	445	ND[a]
MBD-8C	6.11	1.01	.15	453	ND[a]

[a]ND - not determined

SECTION V
RESULTS AND DISCUSSION

The physical and chemical test results and subsequent discussions will be presented in order.

PHYSICAL TEST RESULTS

The physical test results to be discussed pertain to Pope, Loring, and Holloman AFBs materials. The results concern recovered aged binders, modifiers, asphalt-modifier blends, recycled mixtures and binders recovered from accelerated oven-aged recycled mixtures.

Recovered Aged Binders

The properties of the recovered aged pavement (RAP) binders are listed in Table 2 in Section III. Pope AFB is located in a hot and humid climate; Loring AFB is located in a cold and wet environment; while the climate at Holloman AFB is hot and dry. The viscosities were lower than would probably be expected for the age of the pavements. The predominant failure mode was identified to be fatigue at all sites.

Modifiers

Table 3 lists physical properties of modifiers. The viscosity of modifiers at 140°F ranged from 0.08 to 540 P. The flash points ranged from 325°F to 600°F. The lowest flash point modifier underwent the highest weight loss of 29 percent as determined by RTFO procedure in ASTM D-2872.

Asphalt-Modifier Blends

Tables 4, 5, and 6 list physical properties of unaged Pope, Loring, and Holloman AFBs blends. The target viscosities were AC-40, AC-5, and AC-20 for Pope, Loring, and Holloman AFBs, respectively, and all were met satisfactorily. The guide to the acceptability of a blend and its proportions was provided by ASTM D-3381 (Table 1 in Reference 79).

Figures 5, 6, and 7 present a summary of the distribution of effects of modifiers on blend viscosities and show the effects for the Pope, Loring, and Holloman AFBs matrices.

PERCENT AROMATICS \ POLAR/SATURATE	LOW	MED	HIGH	
LOW	MBD-1[a]	MBD-2[b]	MBD-3	< 25%
MEDIUM	MBD-4[a]	MBD-5	MBD-6A[b]	> 25% < 50%
HIGH	MBD-7C	MBD-8C	MBD-9	> 50%
	< 1.0	> 1.0 < 2.0	> 2.0	

[a]High Paraffinic Oils

[b]Soft Asphalts

Figure 4. Holloman AFB Test Matrix.

POLAR/SATURATE / PERCENT AROMATIC	LOW	MED	HIGH	
LOW	MBD-1[a]	MBD-2B[b]	MBD-3B[c]	< 25%
MEDIUM	MBD-4[a]	MBD-5	MBD-6B	> 25% < 50%
HIGH	MBD-7A	MBD-8A	MBD-9	> 50%
	< 1.0	> 1.0 < 2.0	> 2.0	

[a]High Paraffinic Oils

[b]Soft Asphalt

[c]Manufactured Modifier

Figure 3. Loring AFB Test Matrix.

LORING AFB TEST MATRIX

The test matrix was constructed using Loring AFB aged binder as the parent asphalt and nine modifiers to prepare the nine blends for the matrix. Limiting values for the P/S ratio and percent aromatic content were the same as in the Pope AFB test matrix. Six of the modifiers used in the Pope AFB matrix were the same as in the Loring AFB matrix, and three were changed so that the blends would meet the target viscosity. Of these three replacement modifiers, two were commercially available products and used as received. The third modifier was a commercial product from which asphaltenes were removed by NMERI. The new manufactured modifier then met the requirements needed for the target viscosity for the blend and the P/S ratio and percent aromatic content needed for the modifier. Figure 3 illustrates the Loring AFB matrix.

HOLLOMAN AFB TEST MATRIX

The test matrix was constructed using Holloman AFB aged binder as the parent asphalt and eight modifiers to prepare eight blends for the matrix. Position four in the modifier matrix was not filled because no modifier could be found which fit the constraints defined by the limiting values for P/S and percent aromatic content. Six of the modifiers were identical to those used in the Pope AFB test matrix, and two were changed so that the target viscosity could be met. Figure 4 illustrates the Holloman AFB test matrix.

MODIFIER-BLEND DEFINITIONS

For the purpose of this research, modifiers will be defined as MBD-1 through MBD-9. Replacement modifiers will be designated as MBD-6A, MBD-7A and MBD-8A in Figure 2; MBD-2B, MBD-3B and MBD-6B in Figure 3, and MBD-7C and MBD-8C in Figure 4.

The blends will be designated by a combination of the modifier type and the parent asphalt. The parent asphalts are 1, 2 and 3 for Pope, Loring, and Holloman AFBs, respectively. For example, MBD-3B2 is a blend using modifier MBD-3B with Loring AFB asphalt as the parent asphalt. MBD-7C3 is a blend prepared with modifier MBD-7C and Holloman AFB asphalt as the parent asphalt.

TABLE 9. PHYSICAL PROPERTIES OF BLENDS AFTER RTFO (HOLLOMAN AFB)

Blend identi-fication	Pen at 39.2°F, 200 g, 60 s		Pen at 77°C, 100 g, 5 s		Viscosity at 140°F		Ductility 77°F
	0.1 mm	Unaged, %	0.1 mm	Unaged, %	P	Aging index	5 cm/min, cm
MBD-13	26	68	38	58	14,146	7.90	4.5
MBD-23	19	70	46	66	7,525	4.17	8
MBD-33	6	30	31	49	8,321	4.66	11
	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]	---[a]
MBD-53	16	55	46	60	4,598	2.36	26
MBD-6A3	13	46	42	49	7,499	4.05	20
MBD-7C3	20	63	51	65	4,848	2.28	16.5
MBD-8C3	18	69	44	71	5,075	2.55	16
MBD-93	14	61	44	56	4,898	2.29	46
Control	2	100	4	67	380,985	2.20	1.5
ASTM D-3381 AC-20, Table 1	NS	NS	NS	NS	10,200 max	NS	20 min[b]
ASTM D-3381 AC-20, Table 2	NS	NS	NS	NS	10,000 max	NS	50 min[b]

[a] No suitable modifier at hand to fit in matrix.
[b] Specified values are for 77°F.

NOTES: Pen = Penetration
P = Poises
NS = Not specified by ASTM
Control refers to the aged binder recovered from RAP.

control samples is as follows: CTL-1P, CTL-1L, and CTL-1H were prepared by using the aggregates from the Recovered Asphalt Pavements (RAP) from Pope, Loring, and Holloman AFBs, respectively; CTL-2P, CTL-2L, and CTL-2H were prepared using locally obtained fresh aggregate for Pope, Loring, and Holloman AFBs, respectively. The Pope AFB controls were prepared using neat AC-40 asphalt, Loring AFB controls were prepared using neat AC-5 asphalt, and Holloman AFB controls were prepared using neat AC-20 asphalt. The gradation in each mix matrix was kept constant using values established by Lenke et al. (Reference 77). Tables 10 and 11 list the basic properties of recycled mixes and Appendix Tables C-2 and C-3 list resilient modulus test result for 0-day, vacuum-saturated (0-day) and various aging times in an oven at 140°F. The resilient moduli were evaluated at 77 ± 5°F. Figures 8 and 9 present summaries of the moduli data covering the observation period. The results for the effect of vacuum saturation are best represented by damage ratios. Damage ratio is defined as the ratio for resilient modulus at any set of conditions to the initial (0-day) resilient modulus. These ratios varied from 0.80 to 1.15 for all Pope AFB mixes and 0.52 to 1.39 for Loring AFB mixes. According to Lottman et al. (Reference 84) a damage ratio above 0.70 is indicative of low-moisture damage mixes or pavements. Schmidt et al. (Reference 85) reports that the effect of vacuum saturation on resilient modulus is reversible. For damage ratios in excess of unity, this occurrance implies that some modifiers have a beneficial water damage effect to recycled mixtures or could be due to pore pressure. These observations are consistent with Epps et al. (Reference 86), Lottman (Reference 84), Schmidt et al. (Reference 85) and other researchers. In this study, the damage ratios have been noted to increase with increasing polar-to-saturate ratio and percent generic aromatic contents of the modifier. High damage ratio values indicate increased resistance to effects of moisture damage.

The resilient moduli of oven-aged samples indicate that recycled mixes age at a slower rate than virgin mixes. This is consistent with the work of Canessa (Reference 20), Teh-Chang Lee et al. (Reference 87) and others. With the Pope AFB matrix, the aging appeared to decrease as the polar-to-saturate (P/S) ratio increased at the higher percent generic aromatic content. At a lower aromatic content, the reverse was true. In between, the results were inconclusive. For the Loring AFB matrix, aging decreased with an increased P/S ratio in the medium aromatic range but was inconclusive at the high and low aromatic ranges.

TABLE 10. RECYCLED MIX BASIC PROPERTIES (POPE AFB)

Mix identification	Thickness (t)		Bulk specific gravity		Rice specific gravity		Air voids, %	New aggregates,[b] %
	t, in	CV,[a] %	G_b	CV,[a] %	G_{mm}	CV,[a] %		
MBD-11	2.644	0.50	2.162	0.96	2.394	0.25	10.6	5.2
MBD-21	2.484	0.74	2.273	0.26	2.413	0.15	5.8	60.5
MBD-31	2.662	0.68	2.166	1.88	2.369	0.26	8.6	27.8
MBD-41	2.711	0.95	2.108	1.03	2.420	0.80	12.9	0
MBD-51	2.745	0.13	2.127	0.60	2.421	0.79	12.1	1.8
MBD-6A1	2.585	0.18	2.214	0.84	2.370	0.63	6.6	36.7
MBD-7A1	2.695	1.90	2.139	1.36	2.427	0.42	11.8	1.8
MBD-8A1	2.686	0.74	2.144	0.41	2.405	0.51	10.9	5.2
MBD-91	2.709	0.23	2.122	1.07	2.434	0.43	12.8	0.7
CTL-2P	2.655	0.86	2.157	0.92	2.364	0.10	8.7	
CTL-1P	2.579	7.71	2.122	0.49	2.335	0.91	9.1	

[a]CV, % = 100(standard deviation/mean)

[b]Determined based on the procedure in Reference 26.

NOTES: The percent air voids in the RAP was 12-15 percent (Reference 83).
The property values represents an average of three tests.
Thickness represents the dry initial condition.

TABLE 11. RECYCLED MIX BASIC PROPERTIES (LORING AFB)

Mix identification	Thickness (t)		Bulk specific gravity		Rice specific gravity		Air voids, %	New aggregates,[b] %
	t, in	CV, %	G_b	CV, %	G_{mm}	CV,[a] %		
MBD-12	2.465	1.46	2.362	1.33	2.468	---	4.3	9.2
MBD-2B2	2.423	0.88	2.392	0.46	2.454	---	2.5	80.8
MBD-3B2	2.470	0.30	2.358	0.10	2.472	---	4.6	38.8
MBD-42	2.454	0.30	2.361	1.22	2.481	---	4.8	5.6
MBD-52	2.447	1.02	2.351	0.42	2.431	---	5.3	16.5
MBD-6B2	2.452	0.57	2.362	0.32	2.445	---	3.4	42.9
MBD-7A2	2.446	0.10	2.377	0.56	2.465	---	3.6	13.9
MBD-8A2	2.434	0.99	2.377	0.19	2.411	---	1.4	15.4
MBD-92	2.432	1.23	2.382	0.32	2.443	---	2.5	14.9
CTL-1L	2.596	1.58	2.344	0.88	2.437	---	3.8	NA
CTL-2L	2.417	1.77	2.377	0.66	2.429	---	2.1	NA

[a]Not determined.

[b]Determined based on the procedure in Reference 26.

NOTES: Only two tests were run, however, ASTM precision limits were met.
The property values represents an average of three tests.
Thickness represents the dry initial condition.
NA--Not applicable.

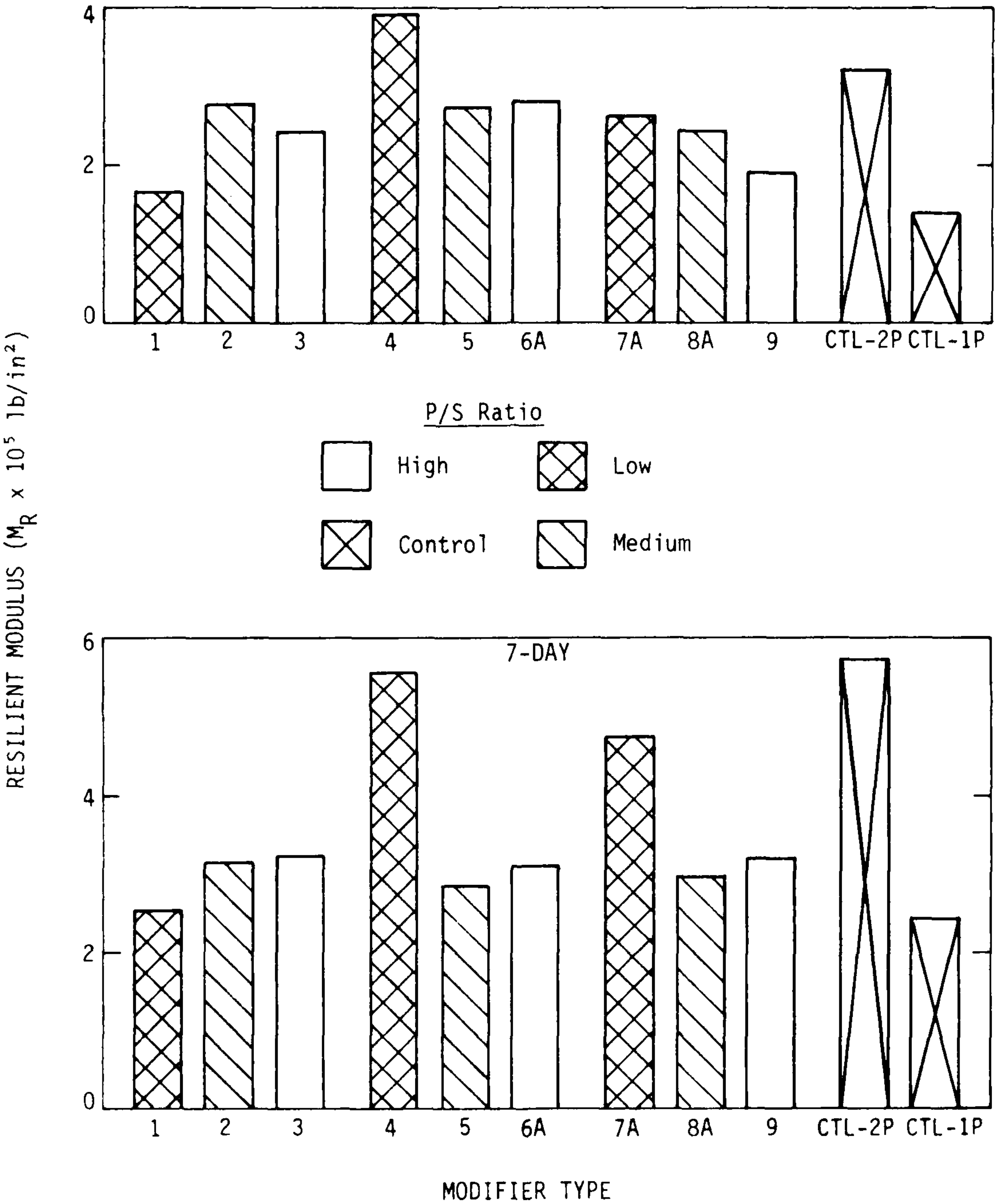

Figure 8. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Pope AFB).

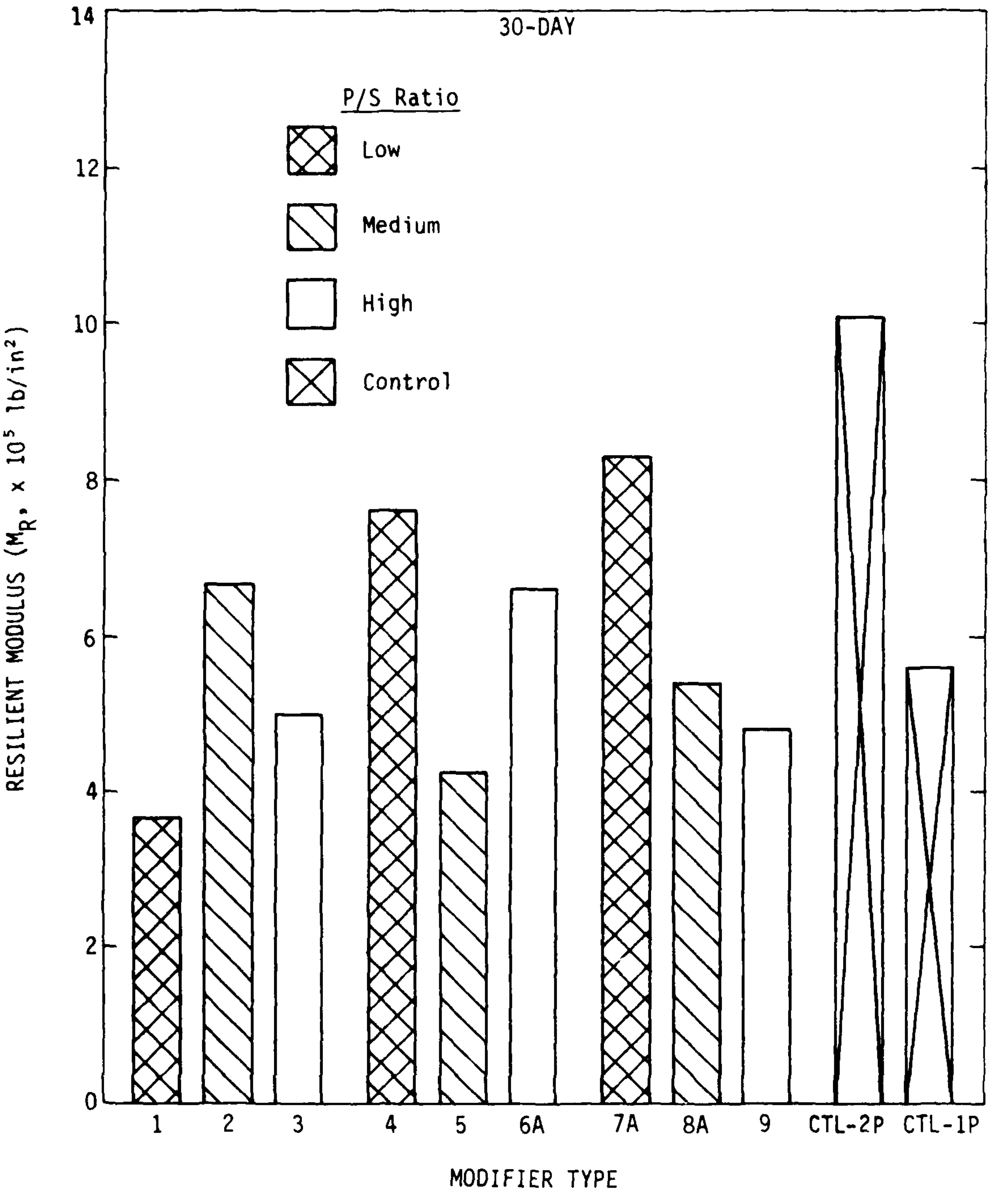

Figure 8. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Pope AFB). (Continued)

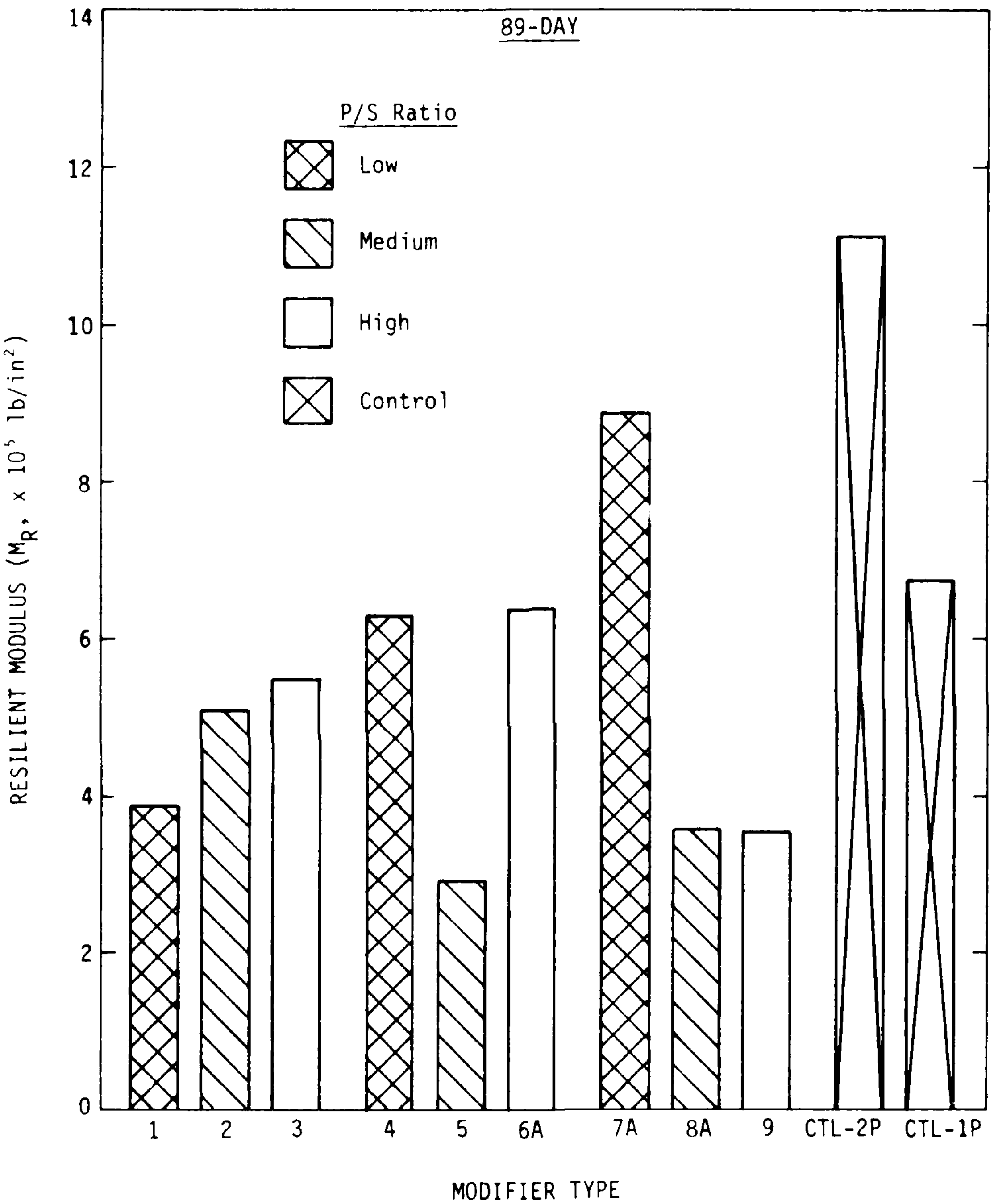

Figure 8. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Pope AFB). (Continued)

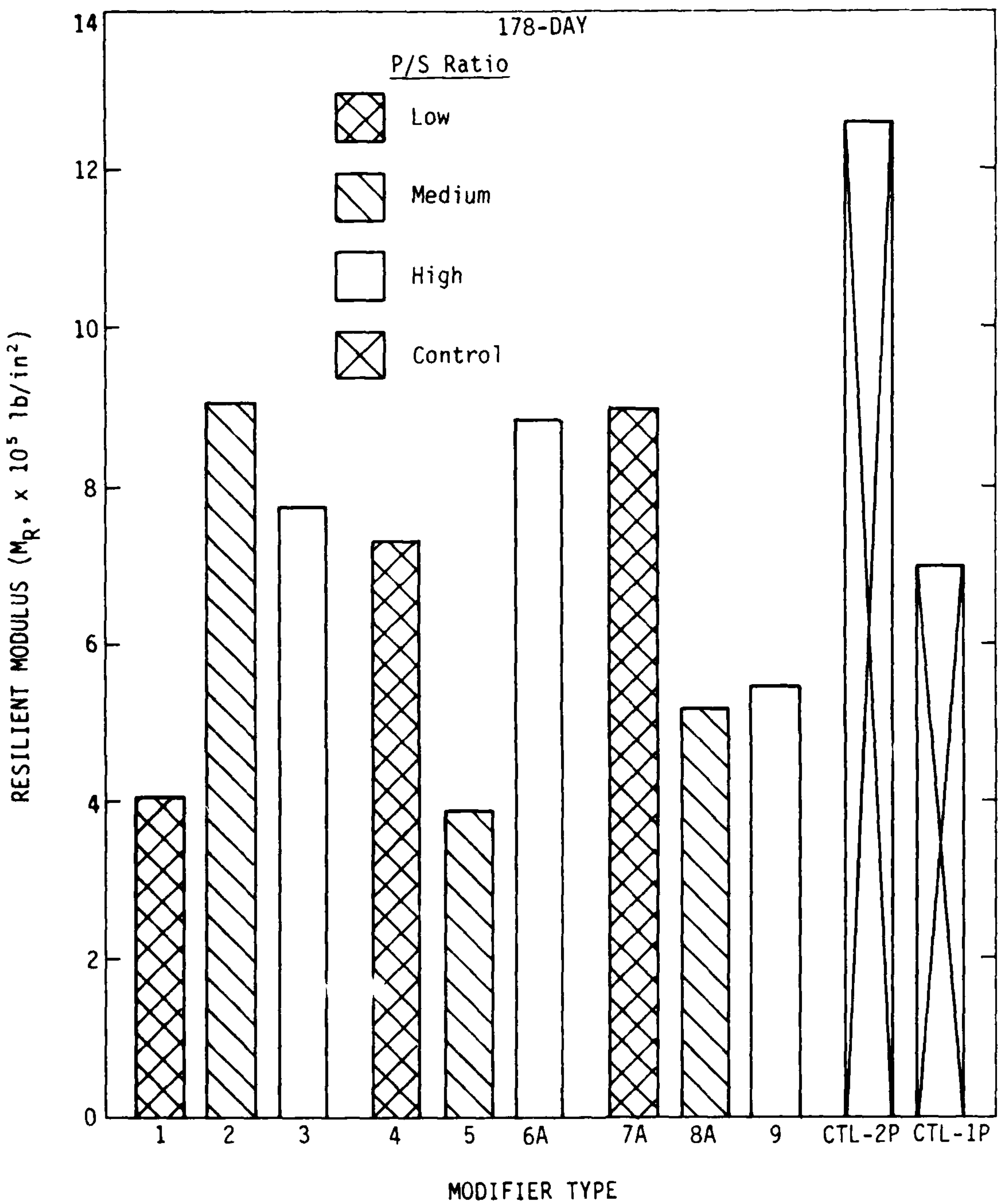

Figure 8. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Pope AFB). (Concluded)

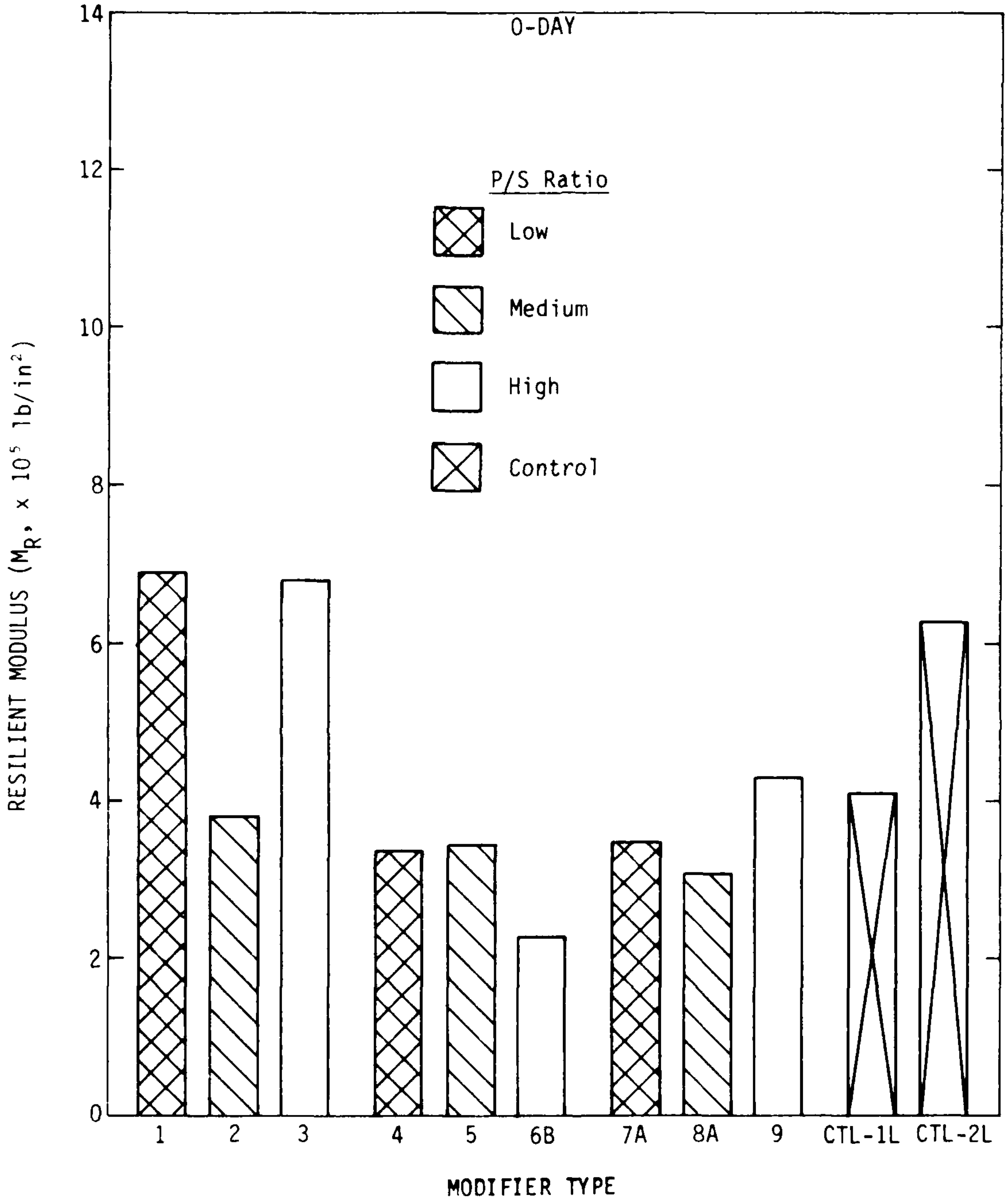

Figure 9. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Loring AFB).

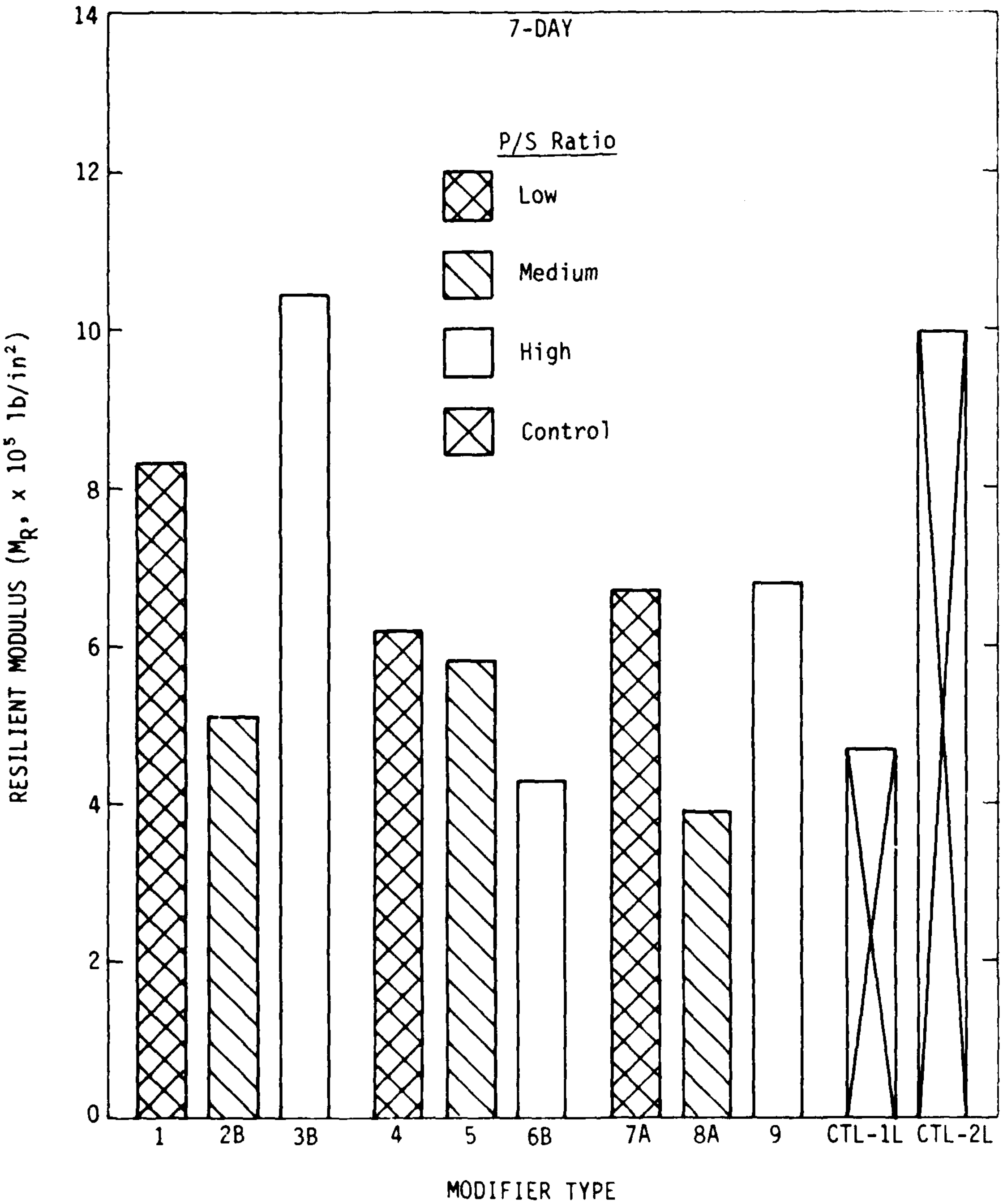

Figure 9. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Loring AFB). (Continued)

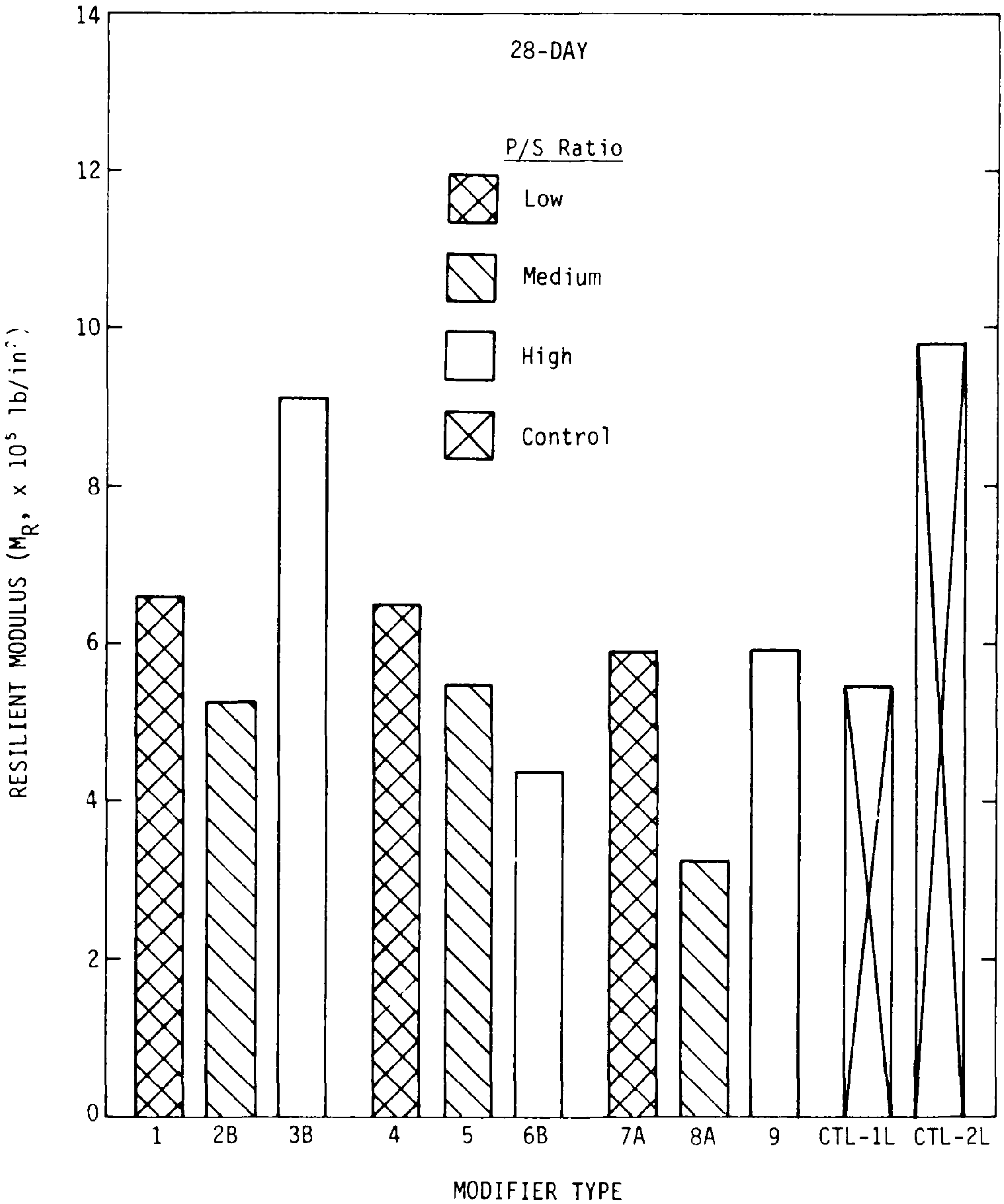

Figure 9. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Loring AFB). (Continued)

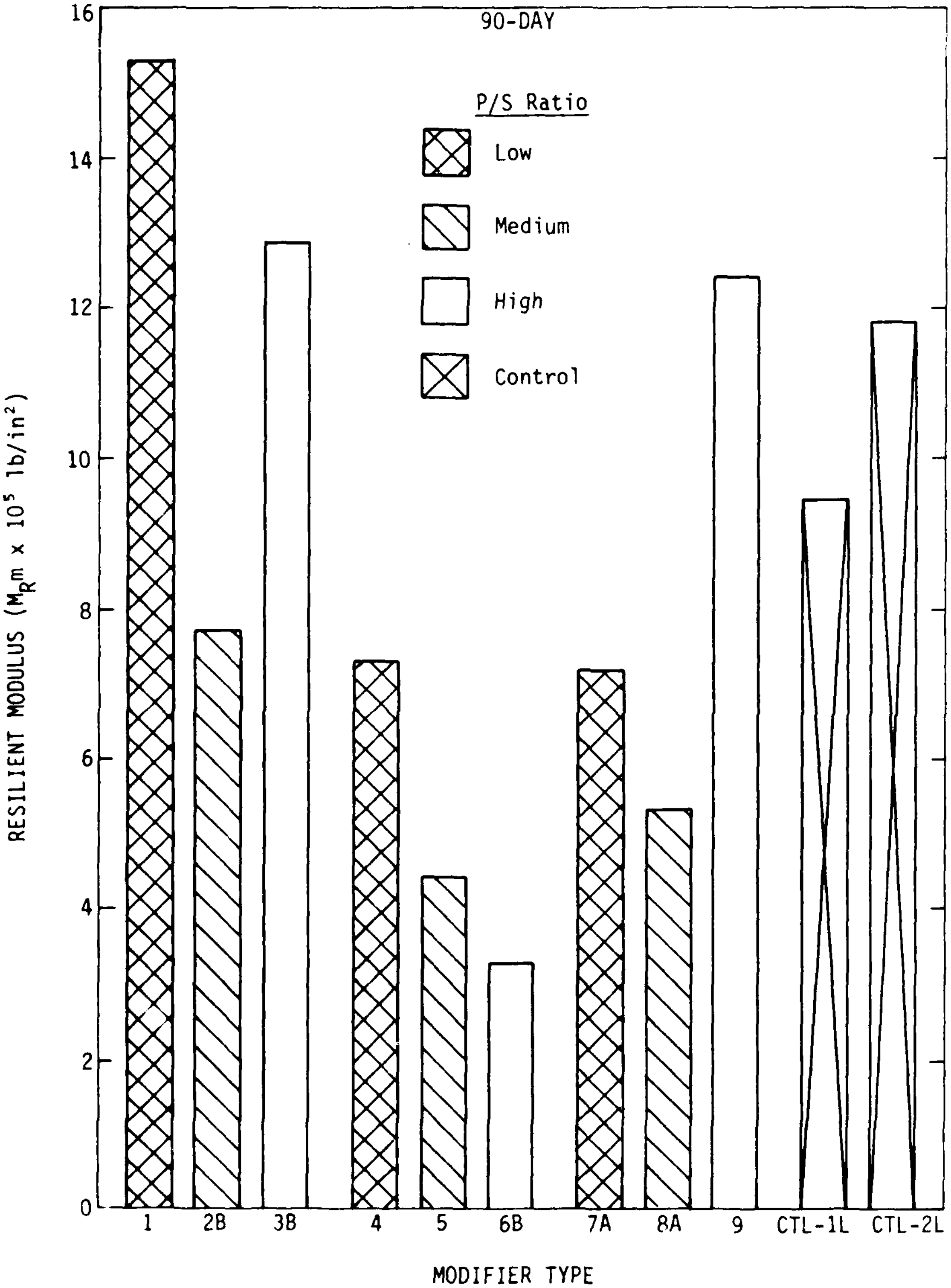

Figure 9. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Loring AFB). (Continued)

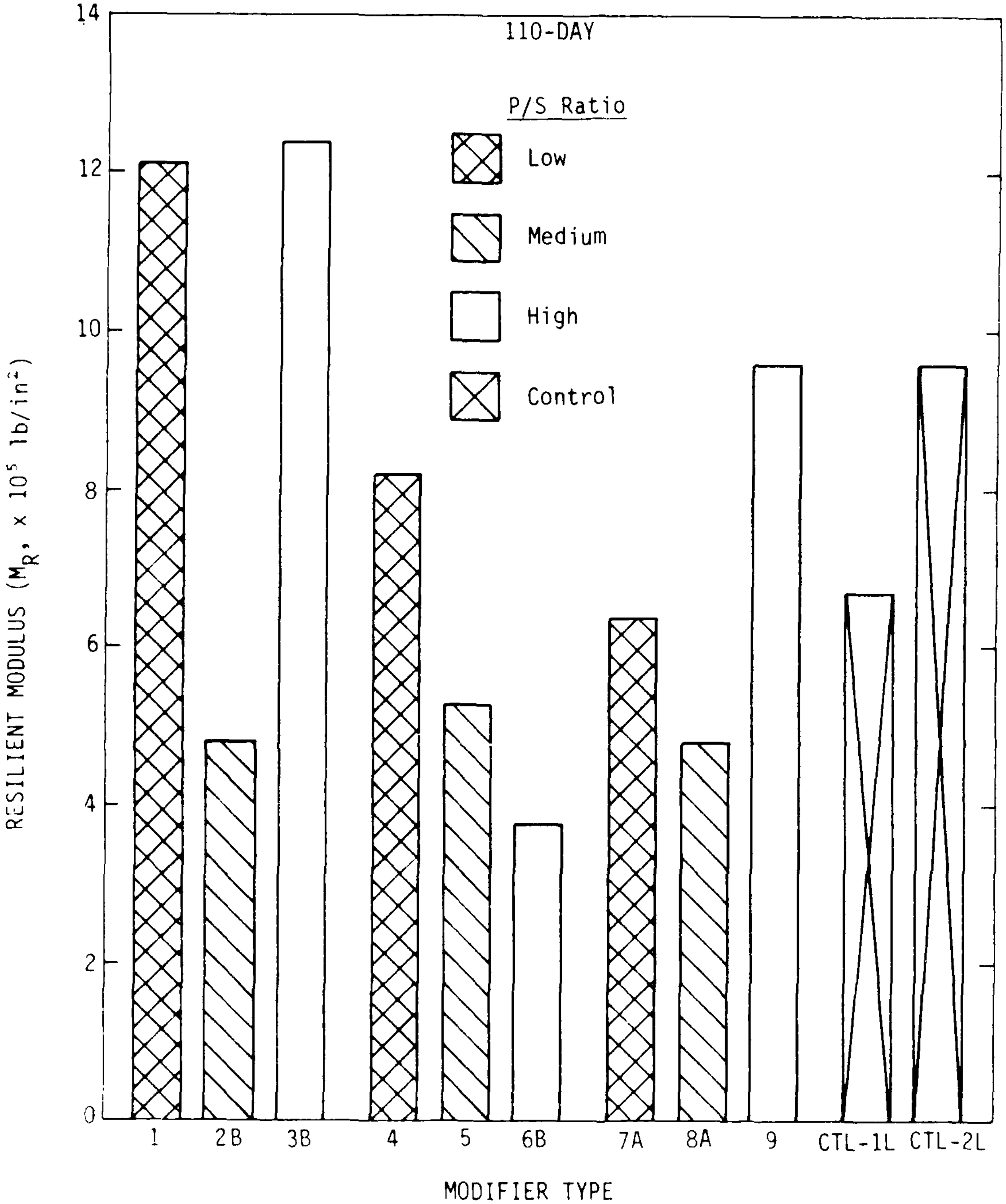

Figure 9. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Loring AFB). (Continued)

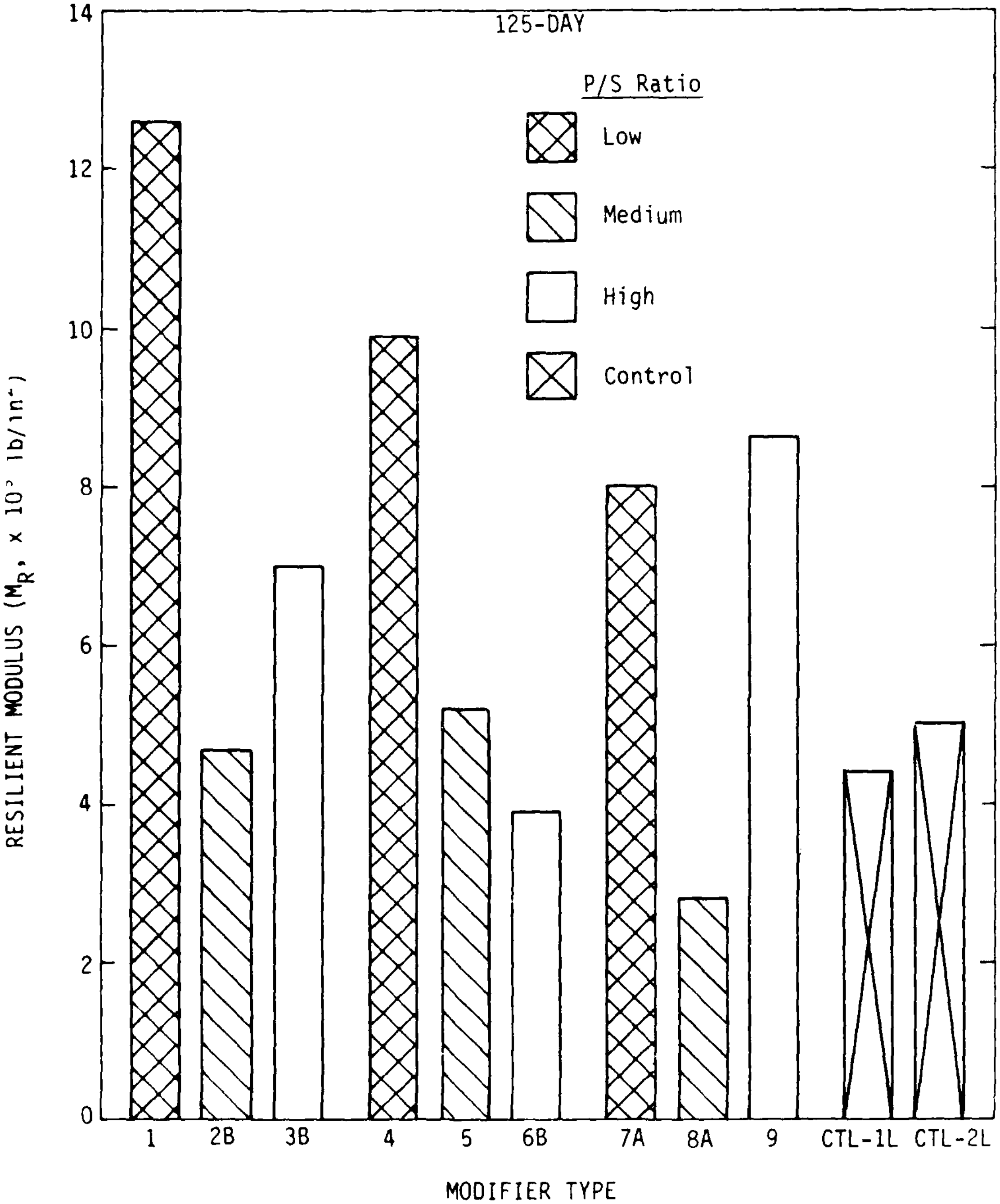

Figure 9. Effects of Modifiers on Resilient Modulus of Recycled Mixes (Loring AFB). (Concluded)

TABLE 24. SOLUBILITY[a] TEST RESULTS (HOLLOMAN AFB--UNAGED)

Blend identification	Heithaus Parameters				Waxman Parameters	
	P_a	P_0	P	X_{min}	T_0	Cot ϕ
MBD-13	0.532	1.455	3.108	2.108	1.985	1.192
MBD-23	0.717	0.899	3.176	2.176	2.669	2.300
MBD-33	0.635	1.336	3.655	2.655	2.806	1.666
MBD-53	0.642	1.284	3.586	2.586	2.767	1.745
MBD-6A3	0.536	1.809	3.898	2.898	3.114	1.051
MBD-7C3	0.563	1.487	3.402	2.402	2.520	1.232
MBD-8C3	0.561	1.484	3.382	2.382	2.470	1.230
MBD-93	0.591	1.495	3.651	2.651	2.688	1.425
Holloman Control	0.651	1.231	3.524	2.524	2.729	1.785
AC-20 Control	0.736	1.155	4.382	3.382	2.450	3.219

[a]Solubility refers to peptization parameter measurements.

TABLE 25. SOLUBILITY[a] TEST RESULTS (HOLLOMAN AFB--RTFO)

Blend identification	Heithaus Parameters				Waxman Parameters	
	P_a	P_0	P	X_{min}	T_0	Cot ϕ
MBD-13	0.505	1.616	3.267	2.267	2.056	1.115
MBD-23	0.704	1.055	3.560	2.560	2.762	2.280
MBD-33	0.530	1.799	3.828	2.828	2.785	1.140
MBD-53	0.628	1.279	3.436	2.436	2.489	1.658
MBD-6A3	0.523	1.824	3.822	2.822	2.842	1.083
MBD-7C3	0.520	1.768	3.682	2.682	2.935	0.964
MBD-8C3	0.536	1.673	3.608	2.608	2.580	1.164
MBD-93	0.627	1.309	3.506	2.506	2.618	1.626
Holloman Control[a]	0.521	1.748	3.650	2.650	2.591	1.108
AC-20 Control	0.749	1.044	4.150	3.150	2.752	3.133

[a]*Solubility refers to peptization parameter measurements

TABLE 22. SOLUBILITY TEST RESULTS (LORING AFB--UNAGED)

Blend identification	Heithaus Parameters				Waxman Parameters	
	P_a	P_0	P	X_{min}	T_0	Cot ϕ
MBD-12	0.171	1.468	1.770	0.770	0.807	0.177
MBD-2B2	0.386	1.935	3.152	2.152	2.355	0.524
MBD-3B2	0.422	1.531	2.651	1.651	1.758	0.679
MBD-42	0.343	1.179	1.795	0.795	0.870	0.486
MBD-52	0.385	1.506	2.449	1.449	1.459	0.616
MBD-6B2	0.515	1.411	2.908	1.908	2.064	0.986
MBD-7A2	0.354	1.445	2.236	1.236	1.289	0.522
MBD-8A2	0.328	1.513	2.252	1.252	1.370	0.429
MBD-92	0.594	1.109	2.727	1.727	1.853	1.401
Loring Control[a]	0.435	1.205	2.135	1.135	1.360	0.656
AC-5 Control	0.682	1.067	3.353	2.353	2.454	2.095

[a]Loring Control refers to aged binder recovered from RAP.

TABLE 23. SOLUBILITY TEST RESULTS (LORING AFB--RTFO)

Blend identification	Heithaus Parameters				Waxman Parameters	
	P_a	P_0	P	X_{min}	T_0	Cot ϕ
MBD-12	0.464	1.586	2.961	1.961	2.183	0.781
MBD-2B2	0.402	1.667	2.789	1.789	1.854	0.641
MBD-3B2	0.576	1.172	2.760	1.760	1.821	0.467
MBD-42	0.217	1.746	2.229	1.229	1.191	0.278
MBD-52	0.497	1.532	3.043	2.043	2.126	0.948
MBD-6B2	0.552	1.567	3.493	2.493	2.740	1.111
MBD-7A2	0.424	1.965	3.411	2.411	1.971	0.922
MBD-8A2	0.325	2.210	3.276	2.276	2.394	0.425
MBD-92	0.411	1.734	2.943	1.943	1.780	0.773
Loring Control[a]	0.238	2.353	3.086	2.086	2.147	0.280
AC-5 Control	0.491	1.846	3.626	2.626	2.336	1.094

[a]Loring Control refers to aged binder recovered from RAP.

TABLE 20. SOLUBILITY TEST RESULTS (POPE AFB--UNAGED)

Blend identification	Heithaus Parameters				Waxman Parameters	
	P_a	P_0	P	X_{min}	T_0	Cot ϕ
MBD-11	0.204	1.750	2.199	1.199	1.252	0.224
MBD-21	0.313	1.678	2.441	1.441	1.117	0.596
MBD-31	0.259	2.085	2.816	1.816	1.798	0.358
MBD-41	0.207	1.884	2.374	1.374	1.465	0.208
MBD-51	0.237	1.800	2.358	1.358	1.355	0.302
MBD-6A1	0.370	1.673	2.655	1.655	1.274	0.760
MBD-7A1	0.338	1.476	2.230	1.230	1.411	0.420
MBD-8A1	0.290	2.179	2.691	1.691	1.757	0.191
MBD-91	0.419	1.070	1.842	0.842	0.911	0.713
Control[a]	0.356	1.316	2.044	1.044	0.901	0.623
AC-40 Control	0.394	1.592	2.626	1.626	1.342	0.775

[a]Aged recovered asphalt treated in the same manner as the blends.

TABLE 21. SOLUBILITY TEST RESULTS (POPE AFB--RTFO)

Blend identification	Heithaus Parameters				Waxman Parameters	
	P_a	P_0	P	X_{min}	T_0	Cot ϕ
MBD-11	0.193	1.636	2.026	1.026	1.068	0.207
MBD-21	0.267	1.892	2.580	1.580	1.497	0.397
MBD-31	0.308	1.995	2.882	1.882	1.887	0.438
MBD-41	0.161	2.113	2.518	1.518	1.546	0.178
MBD-51	0.119	2.074	2.355	1.355	1.250	0.165
MBD-6A1	0.215	2.197	2.797	1.797	1.814	0.264
MBD-7A1	0.153	1.868	2.206	1.206	1.140	0.216
MBD-8A1	0.392	1.019	1.676	0.676	1.438	0.318
MBD-91	0.193	2.213	2.742	1.742	1.711	0.248
Control[a]	0.224	1.942	2.503	1.503	1.586	0.243
AC-40 Control	0.523	1.174	2.464	1.464	1.959	1.263

[a]Aged recovered asphalt treated in the same manner as the blends.

TABLE 18. CLAY-GEL DATA FOR POPE AFB
178-DAY OVEN-AGED MIXTURES

Blend identification	Asphaltenes	Saturates	Aromatics	Polars
MBD-11	37.94	22.66	12.08	27.31
MBD-21	34.06	18.89	13.90	33.15
MBD-31	31.88	12.66	17.04	38.44
MBD-41	45.49	12.63	12.62	29.26
MBD-51	46.34	13.02	16.99	23.57
MBD-6A1	41.31	12.31	15.88	30.51
MBD-7A1	44.37	12.41	16.28	26.95
MBD-8A1	45.36	12.19	16.28	26.17
MBD-91	38.91	11.82	19.42	29.86
CTL-1P	43.50	8.01	12.42	36.08
CTL-2P	43.43	8.24	11.78	36.55

TABLE 19. CLAY-GEL DATA FOR LORING AFB
125-DAY OVEN-AGED MIXTURES

Blend identification	Asphaltenes	Saturates	Aromatics	Polars
MBD-12	30.97	24.42	13.17	31.43
MBD-2B2	29.19	17.13	16.09	37.59
MBD-32	31.56	18.60	12.33	37.51
MBD-42	35.17	15.69	14.50	34.63
MBD-52	28.09	16.71	17.74	37.46
MBD-6B2	22.74	19.43	16.79	41.04
MBD-7A2	28.19	17.11	19.27	35.43
MBD-8A2	26.15	15.85	21.22	36.78
MBD-92	27.29	14.68	20.37	37.65
CTL-1L	34.64	12.25	15.64	37.48
CTL-2L	33.96	12.19	18.90	34.94

additive instead of having the ability to redisperse the asphaltenes like in Pope AFB parent asphalt. On the other hand, blends for Loring AFB and Pope AFB show differences in the calculated versus actual percent polars, with Loring AFB showing these differences in the saturate and aromatic fractions as well. Therefore, it is clear that the modifiers are not additive, but alter the compositional analyses of the total system by redispersing the fractions.

With regard to the 178-day oven-aged recycled mixtures from Pope AFB, the trend continued. MBD-31 had the lowest increase in asphaltene content between RTFO aged and 178 day oven-aged. This particular blend also had the lowest aging index between unaged and RTFO aged blends. In Loring AFB blends, the same blends that exhibited the best physical data also showed only a slight increase in the asphaltene content. Although the Loring AFB parent asphalt could accommodate a wider range of modifiers, the blends prepared with these modifiers offered excellent correlations between the chemical parameters and the physical data. Tables 18 and 19 list the Clay-Gel data for all the oven-aged recycled mixtures.

Compatibility Test Results

Tables 20 through 27 list the test results from the solubility tests. The following observations can be made: asphaltene peptizability (P_a) increases with increasing polar to saturate ratio and increasing percent generic aromatic content of a modifier. The higher the asphaltene peptizability, the lower the peptizing power (P_0) of the maltenes required to keep the asphaltenes dispersed. Most modifiers used in this study reduced the asphaltene peptizability of the blend in comparison to the aged asphalt. These observations are consistent with the findings of Venable et al. (Reference 88). Upon oven-aging of pure blends the asphaltene peptizability generally decreased while the maltene-peptizing power increased as shown in Tables 21 and 23. The increase in the maltene-peptizing power upon aging and/or oxidation is interpreted by Venable et al. as an increased tendency for the oxidized maltenes to be solvents for asphaltenes. The state of Peptization (P) generally increased with aging and this is consistent with discussions held with other asphalt chemists.* The terms X_{min} and T_0 are identical both in dimensional units and magnitude. They are both measures of the smallest quantities of nonpolar solvent required to initiate the least amount

*Personal communication from H. Plancher.

TABLE 17. ACTUAL VERSUS CALCULATED CLAY-GEL DATA ON POPE AFB AND LORING AFB BLENDS

Blend and percent of modifier		Asphaltenes	Saturates	Aromatics	Polars
Pope AFB					
MBD-11	Calculated	36.64	22.56	12.76	28.01
16	Actual	32.90	20.94	15.14	29.74
MBD-41	Calculated	39.29	14.76	15.90	30.04
10	Actual	35.86	13.29	17.60	33.38
MBD-6A1	Calculated	35.06	12.69	18.62	33.60
43	Actual	30.32	11.09	15.86	42.59
Loring AFB					
MBD-2B2	Calculated	22.89	17.35	22.94	36.41
81.5	Actual	21.90	12.36	24.12	41.62
MBD-7A2	Calculated	22.95	16.83	22.48	37.78
17	Actual	22.00	16.95	21.94	39.11
MBD-92	Calculated	22.66	14.07	23.34	39.94
18	Actual	22.20	11.83	24.43	41.54

TABLE 16. CLAY-GEL DATA ON HOLLOMAN AFB BLENDS

Blend identification	Unaged				RTFO aged			
	Asphaltenes	Saturates	Aromatics	Polars	Asphaltene	Saturates	Aromatics	Polars
MBD-13	31.91	20.26	11.85	35.98	30.93	20.68	13.80	34.35
MBD-23	24.13	18.79	16.17	40.90	26.03	18.89	17.53	37.56
MBD-33	21.23	12.15	18.46	48.15	24.05	13.16	16.72	46.06
MBD-53	28.42	14.28	18.16	39.13	27.50	14.24	19.72	38.54
MBD-6A3	28.14	12.87	18.46	40.53	28.68	13.70	19.74	37.88
MBD-7C3	28.04	11.53	22.26	38.29	29.09	12.44	20.99	37.47
MBD-8C3	29.96	13.20	19.36	37.59	27.79	11.09	22.85	38.27
MBD-93	28.96	10.56	19.96	40.52	28.44	10.84	22.13	38.59
Control[a]	35.73	9.37	12.19	42.72	36.38	9.91	12.69	41.65

[a]Control refers to aged binder recovered from RAP.

TABLE 15. CLAY-GEL DATA ON LORING AFB BLENDS

Blend identi-fication	Unaged				RTFO aged			
	Asphaltenes	Saturates	Aromatics	Polars	Asphaltene	Saturates	Aromatics	Polars
MBD-12	23.13	25.09	13.75	38.02	25.70	22.06	14.65	37.60
MBD-2B2	21.90	12.36	24.12	41.62	23.43	11.86	23.42	41.29
MBD-3B2	17.79	18.70	15.22	48.28	18.69	9.48	24.28	47.24
MBD-42	24.89	18.67	16.56	39.88	27.82	11.78	18.02	42.38
MBD-52	22.37	17.80	18.42	41.41	23.57	16.03	22.59	37.80
MBD-6B2	19.00	18.18	18.67	44.15	19.42	10.21	26.40	43.96
MBD-7A2	22.00	16.95	21.94	39.11	24.15	13.77	24.09	38.00
MBD-8A2	22.32	16.07	21.85	39.76	23.24	14.38	25.96	36.12
MBD-92	22.20	11.83	24.43	41.54	23.31	8.89	24.73	43.06
Control[a]	27.61	15.74	14.30	42.33	29.75	12.43	16.33	41.49

[a]Control refers to aged binder recovered from RAP.

TABLE 14. CLAY-GEL DATA ON POPE AFB BLENDS

Blend identi-fication	Unaged				RTFO aged			
	Asphaltenes	Saturates	Aromatics	Polars	Asphaltene	Saturates	Aromatics	Polars
MBD-11	33.33	21.21	15.34	30.13	34.24	22.51	13.39	29.86
MBD-21	26.56	14.79	16.82	41.53	28.01	15.55	15.23	40.53
MBD-31	26.12	11.39	14.26	48.15	30.92	14.34	15.24	39.50
MBD-41	35.86	13.29	17.60	33.38	39.10	12.79	18.75	29.36
MBD-51	33.76	12.27	16.99	36.79	35.95	13.16	16.98	33.54
MBD-6A1	30.32	11.09	15.86	42.59	33.15	12.38	16.06	38.41
MBD-7A1	31.98	11.92	21.33	34.76	34.95	11.24	20.40	33.41
MBD-8A1	30.81	10.60	22.31	36.28	33.69	11.56	23.86	30.90
MBD-91	32.68	10.09	17.00	39.90	35.25	11.56	17.58	35.61
Control[a]	37.70	11.75	15.72	36.25	40.34	12.31	12.72	34.63

[a]Control refers to aged binder recovered from RAP.

CHEMICAL TEST RESULTS

Chemical analyses were performed on recovered aged binder from Pope AFB, Loring AFB, and Holloman AFB, virgin and RTFO recycled blends, modifiers and recovered oven-aged recycled binders. The chemical analyses performed included Clay-Gel analyses, compatibility, HP-GPC Elemental Analyses, Infrared Spectroscopy, Nuclear Magnetic Resonance, and Electron Paramagnetic Resonance.

Clay-Gel Analysis

Modified Clay-Gel analyses were run on all modifiers and also on all materials listed above. Table 1 in Section III lists all data for modifiers alone. Tables 14, 15, and 16 illustrate the data for Pope, Loring, and Holloman AFBs unaged and aged controls and blends, respectively.

General trends can been seen when comparing the unaged blends with the aged blends from Pope AFB and Loring AFB. Upon aging, the asphaltene content increases while the polars decrease. This might be expected since the asphaltene content would be increased with aging. However, in Holloman AFB blends, the asphaltene content remained the same or, in three cases, decreased. This could be attributed to the fact that Holloman AFB asphalt does not age as rapidly as Pope AFB or Loring AFB asphalts, which is also indicated by the aging index.

Another phenomenon that was very pronounced in Pope AFB blends but not in Loring AFB blends was the differences in the calculated values of the percent asphaltenes based on the percent modifier, and the actual percentages of the fractions.

If the modifiers are just additive, then the calculated values for each fraction should be very close to the actual values obtained for each fraction using the Clay-Gel compositional analysis. However, if the modifiers are actually redispersing the asphaltenes, then the calculated values will be different than the actual values. Table 17 illustrates these differences especially for Pope AFB. Note that Loring AFB test results (Table 17) do not show the same trend. It is thought that because the parent asphalt for Loring AFB had fewer asphaltenes to begin with, that the modifiers were

In addition, limited investigations were undertaken to evaluate modifier batch-to-batch effects as well as asphaltenes content on the viscosities at 140°F of resulting blends. This limited study involved a new supply of modifier MBD-7A, the parent modifier for MBD-3B, and Loring AFB aged asphalt. The blends were made at the same modifier percentages used in the original Loring AFB blends. The results showed that batch-to-batch effects were minimal, however increased asphaltene content led to higher blend viscosities. These concluding observations should only be treated in the context of this limited study.

In summary, three field-aged asphalts from three different climatic conditions were involved in this recycling study. Fourteen modifiers from different producers were used to evaluate the physical behavior of recycled blends and mixtures. Characteristic behavior of each modifier was manifest with the type of modifier used and the type of aged asphalt modified. Aging indices at 140°F were highest in the blends made with the highly paraffinic modifiers, namely MBD-1 and MBD-4 in the matrices. Ductilities at 77°F for Pope AFB blends, at 60°F for Pope AFB and Loring AFB blends were lowest for modifiers MBD-1 and MBD-4. Recycled mixes for Pope AFB and Loring AFB are observed to age at a slower rate than virgin mixes. This observation is consistent with published information. The binders recovered from oven-aged recycled mixtures were evaluated for viscosity, using capillary and cone-plate viscometers. The capillary and cone plate viscosity data correlated very well. The results from this section indicate a need for increased research effort towards defining the asphalt-modifier relationship. This definition would indicate the beneficial and or potential damage effects of the various modifiers.

Recycled mixes made in this study were evaluated using the resilient modulus test device for 0, vacuum-saturated, and various aging periods in the oven at 140°F. The results observed in this study are consistent with published work to date.

The next subsection will feature results and discussion from the chemical analyses. These will be presented in the following order: Clay-Gel, Compatibility, HP-GPC, Elemental Analysis, Infrared Spectroscopy, Nuclear Magnetic Resonance, and Electron Paramagnetic Resonance.

TABLE 13. RECYCLED RECOVERED AGED[a] BINDER PROPERTIES (LORING AFB)

Material identification	Modifier, %	Penetration		Viscosity		Ductility
		39.2°F, 200 g, 60 s, 0.1 mm	77°F, 100 g, 5 s, 0.1 mm	140°F, P	275°F, cSt	at 77°F, 5 cm/min, cm
MBD-12	12.5	20	30	49,225	798	3.0
MBD-2B2	81.5	11	33	10,017	571	5.0
MBD-3B2	41	11	18	386,062	2,161	2.5
MBD-42	9	14	26	31,707	2,854	4
MBD-52	19.5	15	40	5,426	423	11
MBD-6B2	45	16	45	2,881	317	100+
MBD-7A2	17	14	34	7,279	477	7.0
MBD-8A2	18.5	18	45	4,364	415	13.0
MBD-92	18	13	37	6,043	448	12.0
CTL-1L	0	10	26	19,259	900	5.5
CTL-2L	0	11	24	40,732	1,343	5.0

[a]Aging time = days at 140°F (oven with a fan).

TABLE 12. RECYCLED RECOVERED AGED[a] BINDER PROPERTIES (POPE AFB)

Material identification	Modifier, %	Penetration		Viscosity			Ductility
		39.2°F, 200 g, 60 s, 0.1 mm	77°F, 100 g, 5 s, 0.1 mm	140°F, P	275°F, cSt	Cone and Plate at 140°F (initial), P	at 77°F, 5 cm/min, cm
MBD-11	16	[b]x	[b]x	[b]x	[b]x	820,000	[b]x
MBD-21	65	10	17	1,045,392	1,971	1,970,000	3
MBD-31	36	8	22	24,696	813	25,500	27
MBD-41	10	4	7	5,827,617	8,146	5,300,000	1.5
MBD-51	13	[c]---	2	[c]---	[c]---	6.39E8	[c]---
MBD-6A1	43	5	11	724,114	3,649	742,000	3.5
MBD-7A1	13	0	9	14,837.009	16,305	16,800,000	0.5
MBD-8A1	16	3	10	908,636	2,617	1,050,000	3
MBD-91	12	2	8	632,573	2,194	780,000	2
CTL-1P	0	0	5	293,967	3,510	402,000	2
CTL-2P	0	0	4	290,797	3,378	382,000	2

[a]Aging time = days at 140°F (oven with a fan).

[b]x - Recovered sample inadequate for routine tests.

[c]Too hard to measure with capillary viscometers.

Recovered Recycled Aged Binders

At the time of this report binder extraction for the Pope AFB and Loring AFB matrices had been completed for 178 days and 125 days in an oven at 140°F. The recovered binders have been physically characterized for viscosity at 140°F; penetration at 39.2°F and 77°F and ductility at 77°F for Pope AFB and 60°F for Loring AFB. The recovered binders from Pope AFB mixes were relatively difficult to evaluate using the capillary viscometers (ASTM D 2171) thus the cone-plate viscometer test method (ASTM D 3205) was adopted to provide a complimentary data set.* The cone-plate test results are summarized in Table 12. The capillary viscometer and cone-plate viscometer data correlated very well with an R value of 0.995. The capillary viscometer data for Loring AFB binders are summarized in Table 13. As may be seen in Table 12, the viscosities of the recovered asphalts decreased with increased polar-to-saturate ratio at each level of aromatic content. The viscosity values from the two controls were identical, indicating that possible asphalt-aggregate interaction effects were identical. The viscosities of recovered asphalts for Loring AFB mixes (Table 13) followed the same trend as per interpretation in Table 12 (Pope AFB mixes). However, the viscosity values for the two controls were dramatically different, indicating that the asphalt-aggregate interaction effects are evident. This difference will probably be noticed in the Clay-Gel composition data to be discussed later.

Miscellaneous Test Results

Weight-loss tests were conducted on a limited basis involving Holloman AFB mixes and using test procedures outlined in ASTM D 2872 test method. The results presented in Table C-4 in Appendix C indicate mixed effects. Some modifiers reduced the weight loss in reference to the control sample while others did not. The weight-loss pattern did not correlate with the aging indices (see Table 9). However, weight loss decreased with increasing ductility after RTFO at 60°F in the low-percent generic aromatic content group. For the medium and high percent generic aromatic contents, weight loss increased with increasing ductility, as shown in Figure C-3 and Table C-4.

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*Mr. V. P. Puzinauskas of the Asphalt Institute performed the Cone-Plate Viscometers Tests.

TABLE 26. SOLUBILITY[a] TEST RESULTS (LORING AFB--RECOVERED, OVEN-AGED[b] BINDER)

Blend identification	Heithaus Parameters				Waxman Parameters	
	P_a	P_0	P	X_{min}	T_0	Cot ϕ
MBD-11 178 day aged	0.314	1.225	1.786	0.786	0.880	0.410
MBD-21 178 day aged	0.490	1.228	2.409	1.409	1.541	0.894
MBD-31 178 day aged	0.365	1.376	2.167	1.167	1.236	0.541
MBD-41 178 day aged	0.336	1.368	2.060	1.060	1.192	0.444
MBD-51 178 day aged	0.306	1.103	1.588	0.588	0.668	0.409
MBD-6A1 178 day aged	0.331	1.329	1.987	0.987	1.044	0.467
MBD-7A1 178 day aged	0.379	1.218	1.962	0.962	1.201	0.493
MBD-8A1 178 day aged	0.379	1.135	1.826	0.826	0.863	0.588
MBD-91 178 day aged	0.337	1.141	1.721	0.721	0.903	0.413
CTL-1P	0.300	1.471	2.101	1.101	1.290	0.330
CTL-2P	0.299	1.520	2.166	1.166	1.317	0.344

[a]Solubility refers to peptization parameter measurements.
[b]Oven-aged at 140°F.

TABLE 27. SOLUBILITY[a] TEST RESULTS (LORING AFB--RECOVERED, OVEN-AGED[b] BINDER)

Blend identification	Heithaus Parameters				Waxman Parameters	
	P_a	P_0	P	X_{min}	T_0	Cot ϕ
MBD-12 125 day aged	0.378	1.753	2.819	1.819	1.968	0.535
MBD-2B2 125 day aged	0.429	1.560	2.733	1.733	1.870	0.686
MBD-3B2 125 day aged	0.500	1.514	3.030	2.030	2.326	0.859
MBD-42 125 day aged	0.431	1.621	2.849	1.849	2.049	0.660
MBD-52 125 day aged	0.412	1.763	3.001	2.001	2.208	0.602
MBD-6B2 125 day aged	0.514	1.492	3.069	2.069	2.197	0.997
MBD-7A2 125 day aged	0.453	1.404	2.566	1.566	1.733	0.737
MBD-8A2 125 day aged	0.402	1.883	3.150	2.150	2.075	0.702
MBD-92 125 day aged	0.467	1.446	2.711	1.711	1.936	0.763
CTL-2L 125 day aged	0.462	1.471	2.736	1.736	1.845	0.804
CTL-1L Control 125 day aged	0.444	1.768	3.177	2.177	2.186	0.790

[a]Solubility refers to peptization parameter measurements

[b]Oven-aged at 140°F

of asphaltene precipitation. The term Cot ϕ represents a measure of solvent charcteristics of the system. The smaller the value of Cot ϕ, the poorer the solvent characteristics of the system. This term was found to be in direct proportion in trend to the asphaltene peptizability.

The solubility test results on recovered oven-aged binders for Pope AFB and Loring AFB which are listed in Tables 26 and 27 indicate that maltene peptizing power and asphaltene state of peptization decreased while the asphaltene peptizability slightly increased or remained unchanged. The comparison is made with the results on unaged blends as listed in Tables 20 and 22. Further effort is required to provide more information and to verify whether the presence of aggregate is the cause for the observation noted above.

Table 28 lists solution properties of five modifiers which were analyzed in this study. MBD-3, performed the best as measured by the lowest aging index and high ductility at 77°F in Pope AFB blends. This modifier had the highest asphaltene peptizability value among the five modifiers. However, the blend MBD-31 had the worst low-temperature susceptibility characteristics in the low-percent generic aromatic group. In this group of modifiers (Table 28), MBD-2B had the poorest solution properties. This modifier produced a blend (Table 8) with the third highest aging index in Loring AFB blends. In Holloman AFB blends, the blend made with modifier MBD-3 had the second highest aging index at 140°F (Table 9).

The results from Heithaus/Waxman analyses can be used to infer compatible asphalt-modifier blends. This information can be obtained initially by observing trends in the plots of Flocculation Ratio (FR) versus Dilution Ratio (DR) as shown in Figure 10. If the curve of the asphalt modifier test results shifts to the right of the curve of the aged binder, this movement implies compatibility. The greater the shift, the more compatible the asphalt-modifier system. Upon RTFO conditioning, generally a leftward shift of the curve from that of an unaged blend is expected (Figure 10). However, most compatible systems may undergo a further rightward shift as shown in Figure 11 (Reference 81 and 89). These movements corresponded to the lowest aging indices for shifts in the rightward direction and highest aging indices for shifts in the leftward direction. Further manifestation of the above compatibility argument is that the aging indices of most of the blends whose curves

TABLE 28. SOLUBILITY[a] TEST RESULTS (MODIFIERS)

Modifier identification	Heithaus Parameters				Waxman Parameters	
	P_a	P_0	P	X_{min}	T_0	Cot ϕ
MBD-2	0.310	1.707	2.472	1.472	1.526	0.421
MBD-2B	0.162	1.500	1.790	0.790	0.808	0.183
MBD-3	0.764	1.091	4.618	3.618	3.265	3.433
MBD-6A	0.703	0.888	2.995	1.995	1.967	2.390
MBD-6B	0.723	1.001	3.616	2.616	2.538	2.644

[a]Solubility refers to peptization parameter measurement.

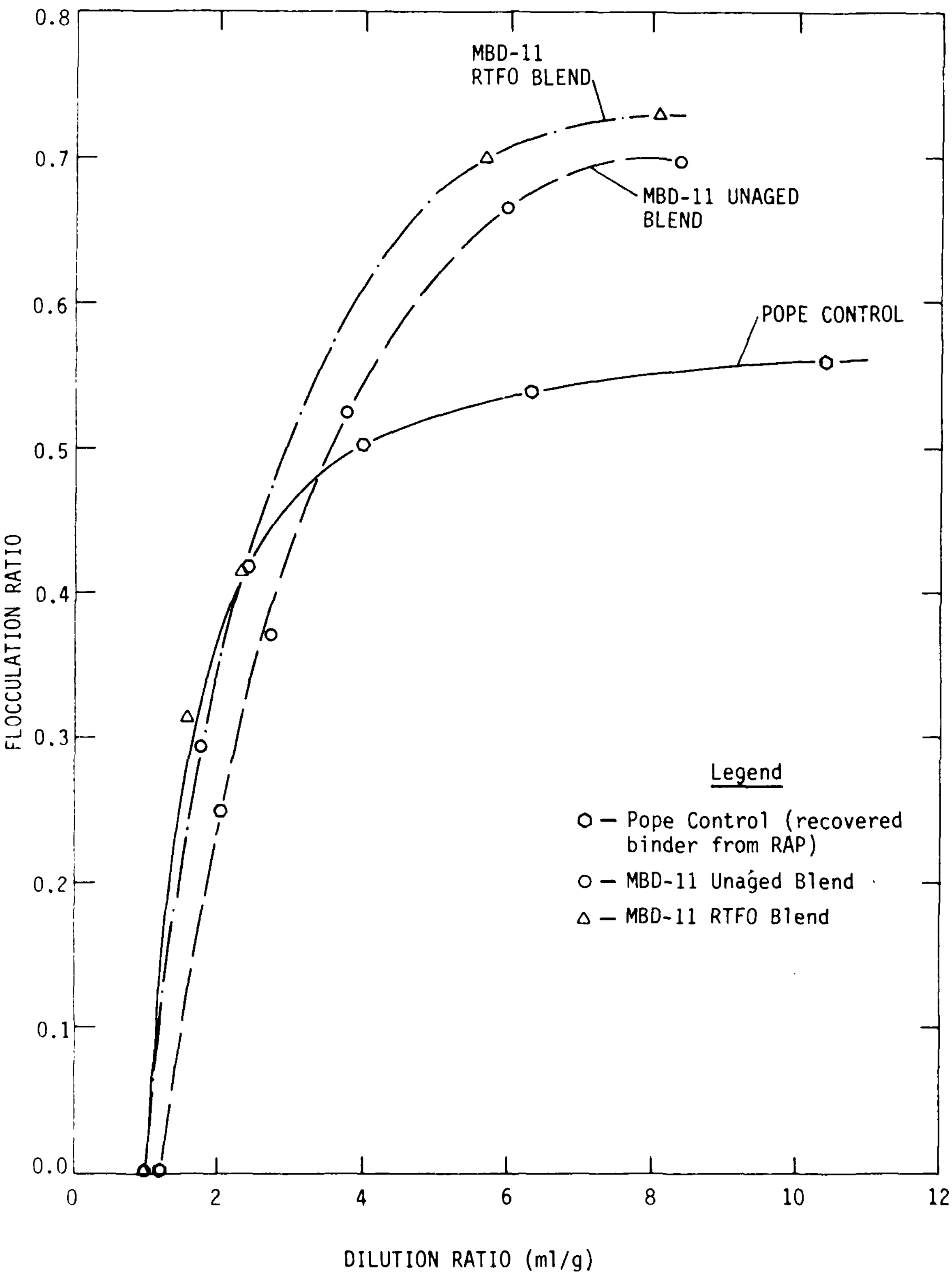

Figure 10. Flocculation Ratio versus Dilution Ratio (Pope AFB).

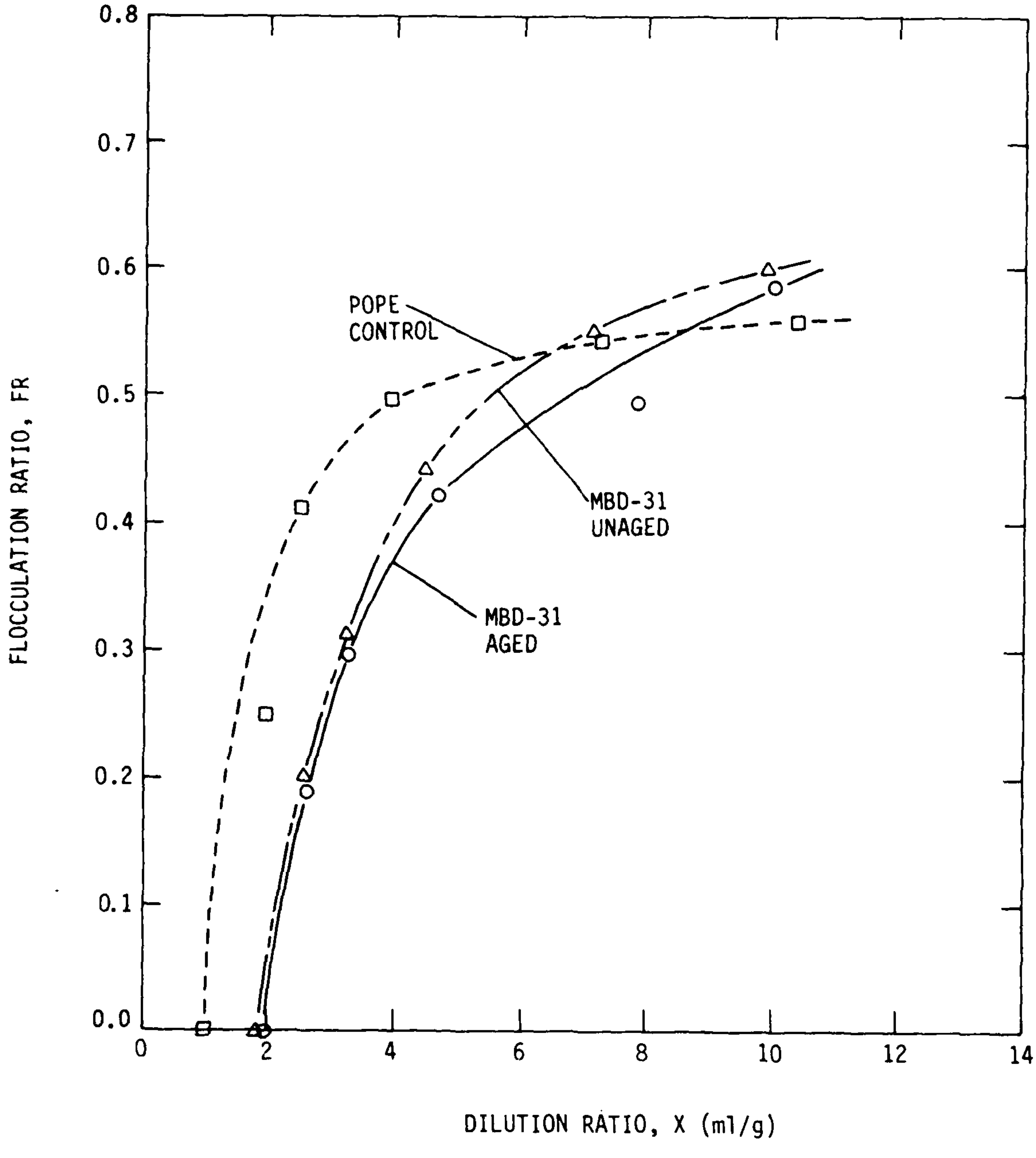

Figure 11. Heithaus Solubility Test Results (Pope AFB).

shifted to the right were less than or very close to the aging index of the parent aged asphalt. Lastly, modifiers with a P/S ratio greater than 0.50 produced the largest rightward shifts in the curves. Ductilities after RTFO at 77°F for Pope AFB blends were highest for all blends with shifts to the right. This trend was generally maintained in Loring AFB and Holloman AFB blends for ductility at 60°F.

The compatibility test results can be presented as Flocculation Ratio versus inverse of Dilution Ratio as shown in Figure 12 and as volume of solvent (polar) versus volume of titrant (nonpolar) solvent as shown in Figures 13 and 14. In the plot of Flocculation Ratio versus inverse of Dilution Ratio, compatibility is measured by a shift to the left of the resulting blend curve with respect to the curve of the aged binder. Figures 12 and 14 present both a compatible and an incompatible asphalt-modifier system. In Figure 13 a compatible system will lead to a shift to the right of the curve as well as a probable decrease in the inclination angle ϕ. In terms of this plot (Figure 13), the following relationship is proposed as a guide in assessing characteristics of a compatible asphalt-modifier system:

$$\text{Cot } \phi = \frac{\Delta T}{\Delta S}_{\text{maximum}} \tag{9}$$

where ΔT = change in nonpolar solvent/gram asphalt, and

ΔS = change in polar solvent/gram asphalt.

Modifier MBD-3 in Table 27 satisfied the above formulation in test Pope AFB blends. In test with Loring AFB blends, modifier MBD-6B with a cot ϕ of 2.644 produced more compatible blends than modifier MBD-2B whose cot ϕ value is 0.133. In Holloman AFB blends, modifiers MBD-3 and MBD-2B did not perform well as per results listed in Table 9.

On the contrary the compatibility test results in this study have indicated no universal modifier for all aged asphalt systems. For example, the modifier matrix (Figure 4) used for blends involving Holloman AFB aged asphalt included modifier MBD-3 which turned out to be the best for Pope AFB blends. This modifier did not live up to the expectation in Holloman AFB blends, as shown in Table 9, in comparison to the results in Table 7. For Holloman AFB blends, modifiers MBD-2, 5, and 9 would be chosen based on compatibility, although based on ductility the choices would be MBD-9, 5, and 6A, respectively. Using the aging index MBD-9, would offer the best choice. This

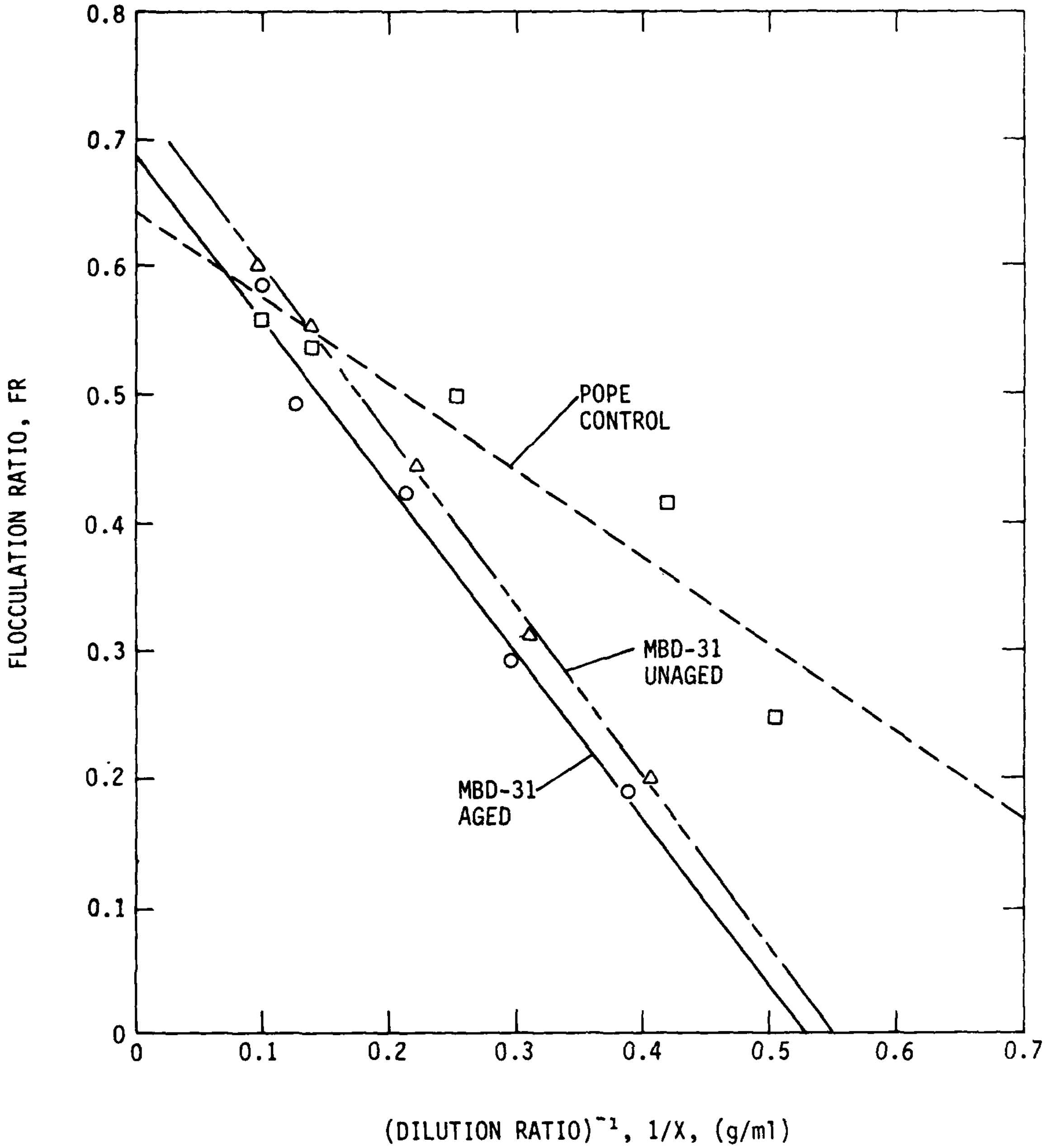

Figure 12. Heithaus Solubility Test Results (Pope AFB).

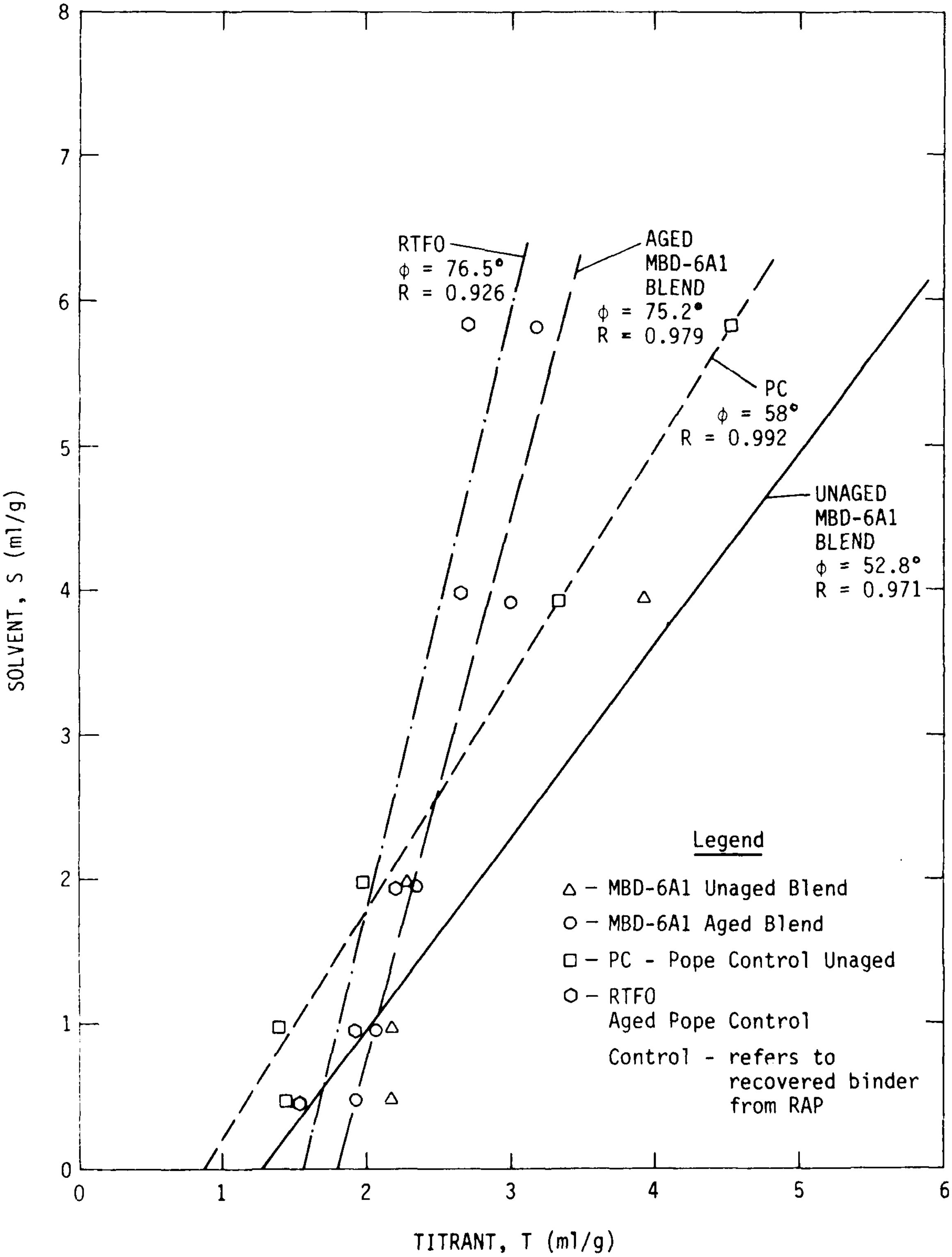

Figure 13. Waxman Solubility Test Results (Compatible Blend) (Pope AFB).

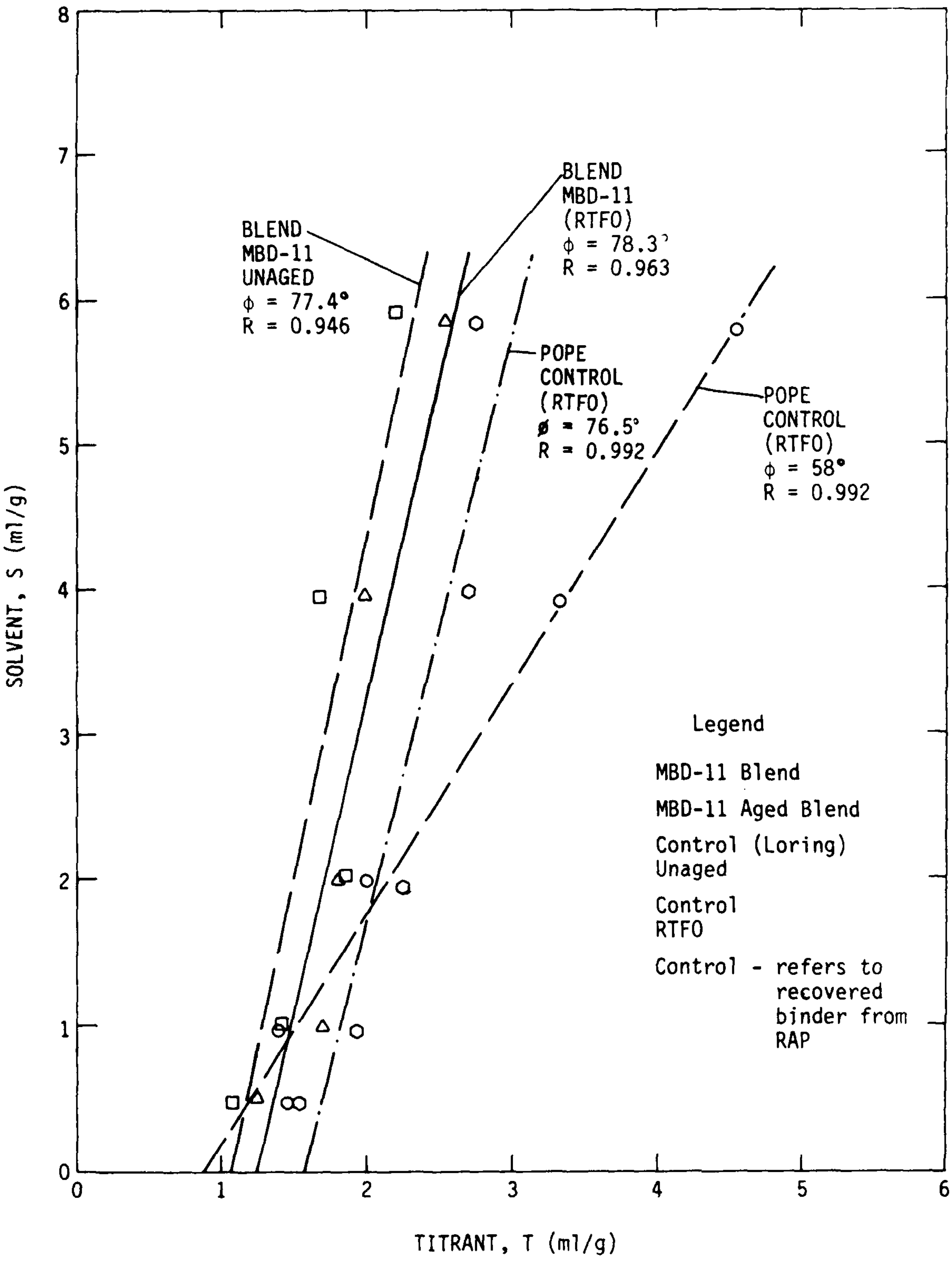

Figure 14. Waxman Solubility Test Results (Incompatible Blend) (Pope AFB).

deduction supports the earlier observations that modifiers with increasing P/S ratio and increasing percent generic aromatic content are generally more preferred.

In summary, compatibility tests developed in this study are proposed. From these tests, asphaltene peptizability, maltene peptizing power, state of peptization and other solution properties can be assessed. The shifts in the resulting curves from the test results can be used to judge compatibility of candidate products. The solubility test results indicate that one asphalt rejuvenator material may work best for one aged asphalt and another for a second aged asphalt. RTFO conditioning of blends can also provide more information about the resulting blend, especially in interpreting compatibility after heat treatment. Some blends can look compatible before heat treatment but might fall apart due to the action of heat. Performance properties such as aging index and ductility have been used to substantiate the proposed compatibility hypothesis. There is need for more research effort to substantiate the above proposed procedures.

The following section will feature results and discussions of test results from HP-GPC analyses.

High-Pressure Gel Permeation Chromatography

HP-GPC data were obtained on all aged binders, RTFO aged binders, modifiers, and unaged and RTFO aged blends for the Pope AFB and Loring AFB matrices. In addition, in the Pope AFB matrix, the asphaltenes and maltenes were also analyzed separately. The samples were sent to Dr. P. W. Jennings at Montana State University for analyses where a 17-state pooled-fund project is in progress, using HP-GPC.

As stated previously in this report, HP-GPC is a separation technique that separates a sample based on molecular size. Three regions are designated: large molecular size (LMS), medium molecular size (MMS), and small molecule size (SMS). A chromatogram is obtained which is a plot of response measured in millivolts versus time. The cutoff points for each region are based on the time a particular size material takes to travel through the column with the LMS eluting first, then MMS and finally SMS. A sample of a chromatogram is shown in Figure 15. The cut times are shown on this chromatogram as well. The peak areas and percentages of LMS, MMS, and SMS are then calculated (Reference 41).

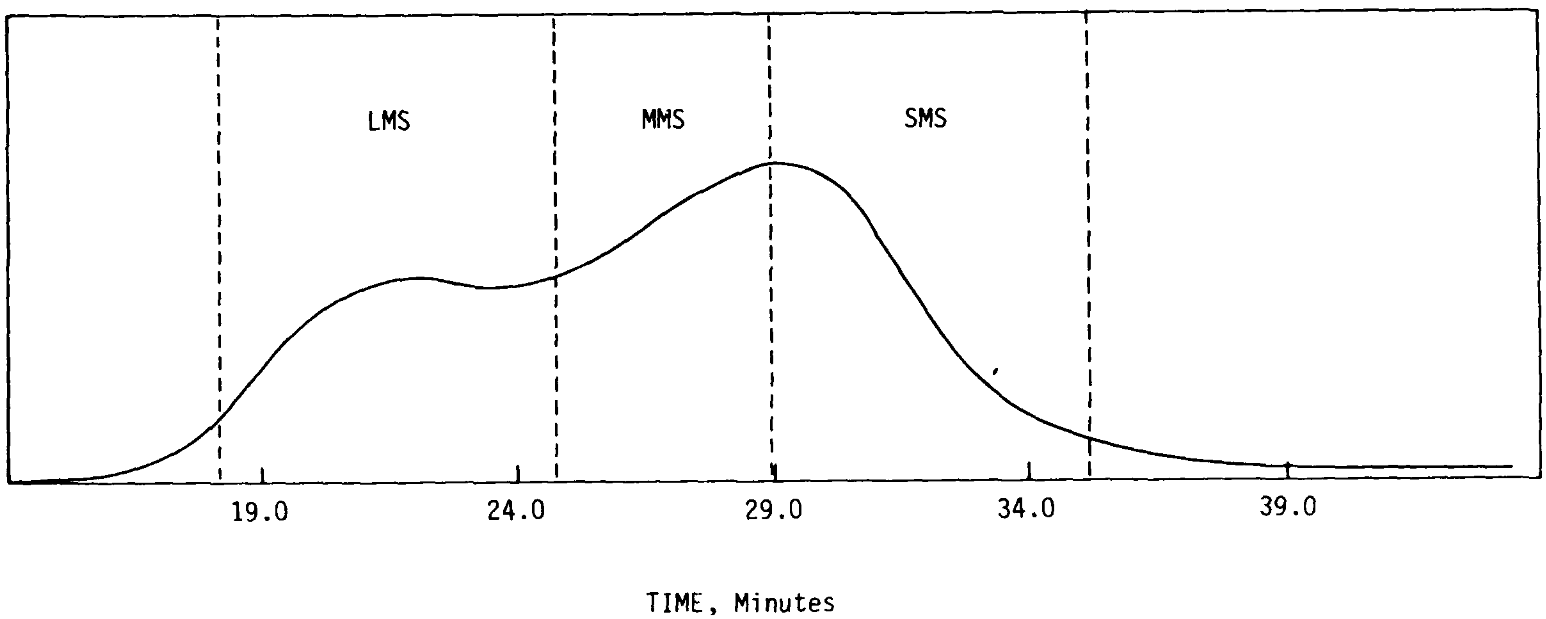

Figure 15. HP-GPC Chromatogram (Pope AFB).

If a "model" pavement is available, then comparisons can be made between the "model" chromatogram and the aged binder.* Usually the aged binder has more LMS material due to possible agglomeration of polar components and less MMS and/or SMS than the "model." In recycling the aged binder, a modifier should be chosen that will reduce the LMS region and thus the above mentioned aglomeration and increase the MMS and/or SMS. The prepared blend should then have a chromatogram close to the model. Without a model, as in this research effort, a reduction in LMS and addition in MMS and SMS are still valid, however, no model is available for comparison purposes.

Table 29 lists the HP-GPC data for all modifiers used in Pope AFB and Loring AFB matrices. Tables 30 and 31 list the data for Pope AFB and Loring AFB unaged and RTFO aged blends,respectively. The two controls are the Pope AFB aged binder and Loring AFB aged binder for the respective matrix.

The Pope AFB aged binder was very high in LMS. It was felt that it needed MMS material and a small amount of SMS (Reference 83). Several modifiers could add MMS and SMS, such as MBD-2, MBD-6A, and MBD-3, but MBD-2 and MBD-6 would also add too much LMS to be satisfactory. Therefore, based only on HP-GPC data, Pribanic et al. (personal letter communication) suggested that MBD-3 should be the modifier of choice to restore the aged binder.

In the Loring AFB aged binder, the LMS percentage was considerably lower than in Pope AFB binder. However, since this pavement was also cracked and needed recycling a reduction in LMS was needed, with a small increase in SMS. Modifiers MBD-6B, MBD-2B, and MBD-3B would decrease the LMS, with MBD-3B increasing the SMS by the smallest amount while also decreasing the LMS by the largest amount. Based on HP-GPC data alone, MBD-3B would be the modifier best suited to improve the aged binder and restore it to an acceptable condition.

The following subsections will cover elemental analysis, Infrared Spectroscopy, Nuclear Magnetic Resonance, and Electron Paramagnetic Resonance.

<u>Elemental Analysis</u>

Samples of all aged binders, and all unaged and RTFO aged blends were sent to the Chemistry department at the University of New Mexico for percent

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*Personal communication from W. P. Jennings.

TABLE 29. HP-GPC DATA
MODIFIERS ALONE

Modifier identification	LMS	MMS	SMS
MBD-1	0.0	0.0	100.0
MBD-2	23.2	53.2	23.6
MBD-2B	14.9	47.2	37.9
MBD-3	3.4	42.4	54.2
MBD-3B	6.2	54.3	39.5
MBD-4	0.0	0.0	100.0
MBD-5	0.0	3.7	96.3
MBD-6A	21.9	40.1	38.0
MBD-6B	5.1	41.1	53.8
MBD-7A	0.0	0.0	100.0
MBD-8A	0.0	7.6	92.4
MBD-9	0.0	0.3	99.7

TABLE 30. HP-GPC DATA FOR POPE AFB BLENDS

Blend identification	UNAGED			AGED		
	LMS[a]	MMS[a]	SMS[a]	LMS[a]	MMS[a]	SMS[a]
MBD-11	34.0	35.5	30.6	39.4	34.2	26.4
MBD-21	31.3	39.5	29.2	33.9	38.3	27.8
MBD-31	30.5	38.3	31.2	31.0	38.0	30.9
MBD-41	38.8	35.1	26.1	40.6	33.8	25.6
MBD-51	36.3	34.0	29.8	35.8	34.2	30.0
MBD-6A1	36.3	38.5	25.2	40.6	33.8	25.6
MBD-7A1	36.8	34.1	29.1	37.8	33.5	28.7
MBD-8A1	36.2	33.8	30.0	39.3	32.1	28.6
MBD-91	39.2	33.8	27.0	40.7	32.7	26.6
Pope Control[b]	38.1	35.9	26.0	40.2	34.5	25.3

[a]These are percentages of material using an UV detector at a wavelength of 340 mm.

[b]The control refers to the aged binder recovered from the RAP.

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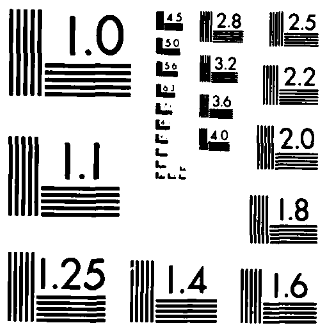

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TABLE 31. HP-GPC DATA FOR LORING AFB BLENDS

Blend identification	UNAGED			AGED		
	LMS[a]	MMS[a]	SMS[a]	LMS[a]	MMS[a]	SMS[a]
MBD-12	24.1	44.6	31.3	27.6	41.8	30.6
MBD-2B2	17.9	46.5	35.6	22.8	44.0	33.2
MBD-3B2	19.6	47.4	33.0	22.9	45.9	31.2
MBD-42	24.3	44.2	31.5	27.6	41.6	30.8
MBD-52	23.9	41.6	34.5	24.4	39.5	36.1
MBD-6B2	18.7	43.2	38.1	21.8	42.3	35.9
MBD-7A2	22.6	42.3	35.1	22.4	40.2	37.4
MBD-8A2	21.7	41.1	37.2	24.4	38.7	36.9
MBD-92	20.9	40.5	38.6	24.0	38.8	37.2
Loring	24.4	44.5	31.1	---	---	---
Control[b]	24.3	44.4	31.3	27.5	42.5	30.0

[a]These are percentages of material using an UV detector at a wavelength of 340 nm.

[b]The control refers to the aged binder recovered from the RAP.

carbon, hydrogen, and nitrogen analyses. Table 32 lists all data for Pope AFB blends, unaged and aged, and Table 33 lists data for Loring AFB blends, unaged and aged. There were basically no significant differences in the carbon/hydrogen ratio throughout the blends. Also, no significant differences in the carbon/hydrogen ratio were observed between unaged and RTFO aged blends in either matrix.

Infrared Spectroscopy (IR)

Functional group analysis of Loring, Pope, and Holloman AFBs, control samples were conducted using differential IR. The analysis included field-aged recovered asphalts (controls), unaged blends, RTFO-aged blends, and modifiers. This analysis yields concentration data for compounds absorbing in the carbonyl region and sulfoxides. These compounds which represent oxidation products in asphalts yield information regarding the extent of aging.

Our samples exhibited an unknown band at 1718 cm^{-1} which is a potentially hydrolyzable (reacts with water to give a carboxylic acid or the carboxylic acid salt) functionality. Normally the major hydrolyzable components are acid anhydrides of the 1, 8-naphthalic type (Referencc 67). This 1718 cm^{-1} band (probably due to the presence of aromatic esters) is present in all samples studied thus far. Experiments are now underway to determine the source of these esters, which include looking at solvent and temperature effects on the differential IR spectra.

Nuclear Magnetic Resonance (NMR)

Previous attempts at solution-state NMR analysis of aged pavements yielded little useful information. It was therefore necessary to attempt to obtain solid-state spectra leading to information regarding the relative amounts of saturates and aromatics (Reference 92).

At this point in the study, the NMR facility at Colorado State University has been contacted regarding the solid state NMR spectra of asphalts involved in this study. At this time, NMERI personnel are negotiating for the use of their facility.

Electron Paramagnetic Resonance

Some preliminary investigation into the utility of Electron Paramagnetic Resonance (EPR) was undertaken. As stated earlier in this report, a separate

TABLE 32. ELEMENTAL ANALYSIS DATA FOR POPE AFB BLENDS

Blend identification	Unaged			Aged (after RTFO)		
	Carbon, %	Hydrogen, %	Nitrogen, %	Carbon, %	Hydrogen, %	Nitrogen, %
MBD-11	82.02	9.44	none	83.03	10.43	0.23
MBD-21	83.64	10.42	0.34	85.05	10.00	0.56
MBD-31	83.83	10.28	0.44	84.49	10.55	0.39
MBD-41	82.20	9.89	0.21	83.67	9.86	none
MBD-51	82.51	9.69	0.25	83.79	9.88	none
MBD-6A1	83.85	11.24	0.33	83.35	10.47	none
MBD-7A1	83.69	10.11	0.25	84.07	10.05	none
MBD-8A1	84.04	11.40	0.29	83.98	10.25	<0.2
MBD-91	82.23	6.68	0.38	83.57	9.93	<0.07
Control[a]	82.84	9.77	none	83.13	9.94	0.16

[a]Control refers to the aged binder recovered from the RAP.

TABLE 33. ELEMENTAL ANALYSIS FOR LORING AFB BLENDS

Blend identification		Carbon, %	Hydrogen, %	Nitrogen, %
MBD-12	Unaged	85.02	10.47	0.48
	RTFO	84.54	10.62	0.43
MBD-2B2	Unaged	82.71	10.18	0.49
	RTFO	84.85	10.22	0.80
MBD-3B2	Unaged	84.88	10.44	0.46
	RTFO	85.68	10.62	0.63
MBD-42	Unaged	84.80	10.34	0.50
	RTFO	84.55	10.36	0.46
MBD-52	Unaged	85.16	10.43	0.48
	RTFO	85.07	10.20	0.51
MBD-6B2	Unaged	85.26	10.42	0.58
	RTFO	85.29	10.27	0.62
MBD-7A2	Unaged	85.00	10.27	0.48
	RTFO	85.14	10.12	0.56
MBD-8A2	Unaged	84.66	10.19	0.53
	RTFO	84.38	10.20	0.43
MBD-92	Unaged	85.76	9.98	0.52
	RTFO	85.11	9.99	1.11
Control	Unaged[a]	84.27	9.90	0.62
	RTFO	84.17	9.71	0.29

[a]Control refers to the aged binder recovered from the RAP.

project utilizing EPR is currently underway, therefore, no data will be included in this manuscript at this time.

CORRELATIONS

One of the objectives in using the physical and chemical methods to characterize aged asphalts, modifiers, and blends was to identify useful chemical and physical parameters which can be incorporated into a modifier selection specification. In this section, correlations which have been developed between the chemical parameters and physical properties will be presented.

Modifier Type

The effects of the same modifier to varying aged asphalts is shown in Figure 16 (Reference 89). In this figure, Pope AFB blends aged more severely than Holloman AFB and Loring AFB blends. These results further indicate that Loring AFB aged asphalt accommodates a wider range of modifiers than Holloman AFB and Pope AFB aged asphalts. The aging index decreases with increasing percent generic aromatic content as seen by the variation from MDB-1, MBD-4, and MBD-7A in the low P/S ratio.

The NMERI research personnel conducted analyses of published data (Reference 33) using the format developed in this research effort. These published data were obtained on two well-recognized extreme asphalts, namely, California coastal and California valley. The NMERI analyses indicated that the pattern reported above on Pope AFB and Loring AFB blends with respect to modifier type are typified by the recycled blends made using California coastal and California valley asphalts. That is, the blends made using the latter two asphalts on a set of modifiers show that California coastal is more selective of a suitable modifier than California valley asphalt. In fact, California valley asphalt, just like Loring AFB aged asphalt, accommodates a wide range of modifiers. The difficulty in recycling California coastal asphalt has been noted by the research effort of Puzinauskas (Reference 93) and other researchers.

Ductility

Ductility after RTFO is a performance variable which was observed to be very sensitive to the changes in the chemistry of the modifier. Figures 17 (Reference 81), C-1 and C-3 summarize the results with respect to changing

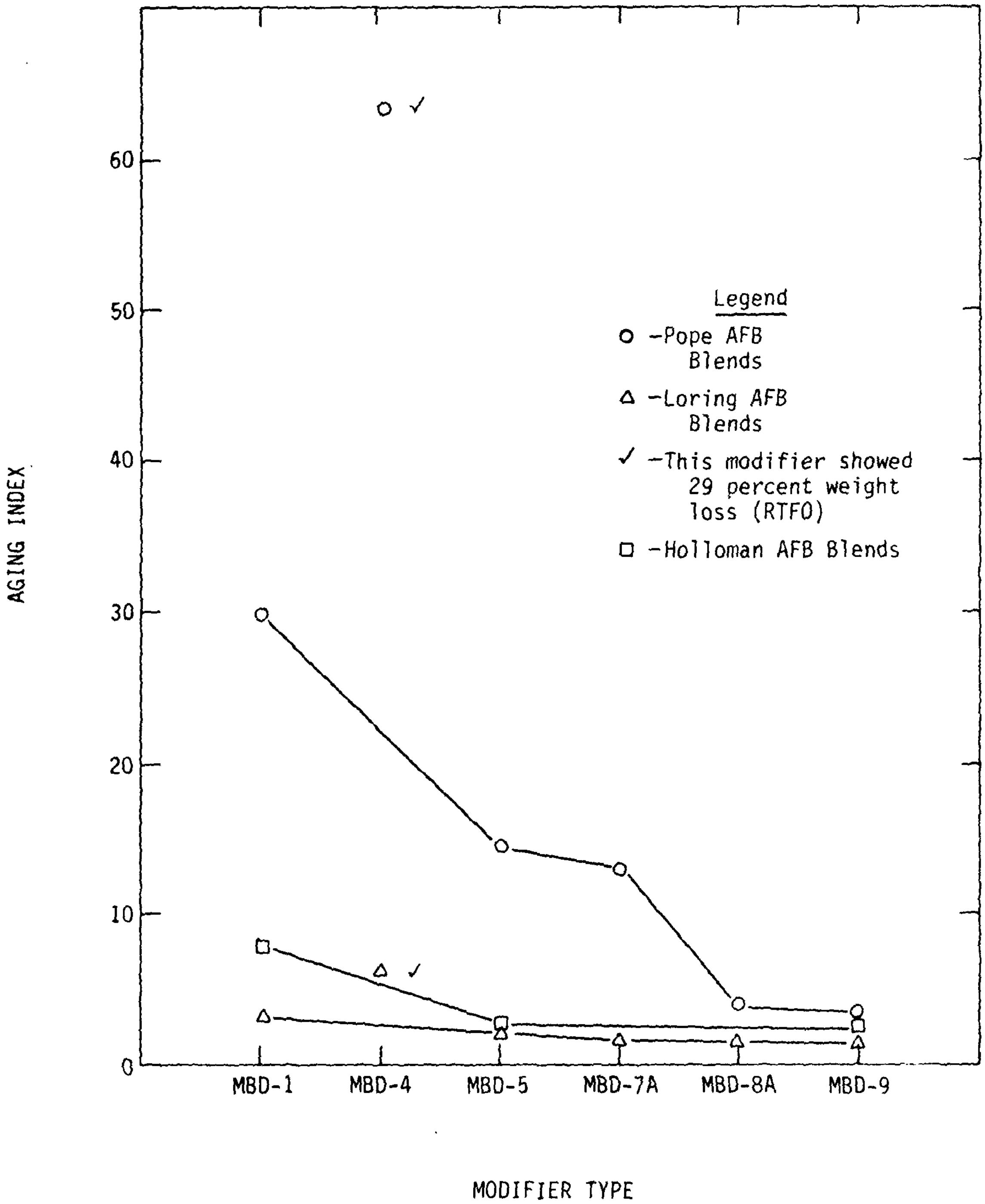

Figure 16. Blend-Aging Index versus Modifier Type (Reference 89).

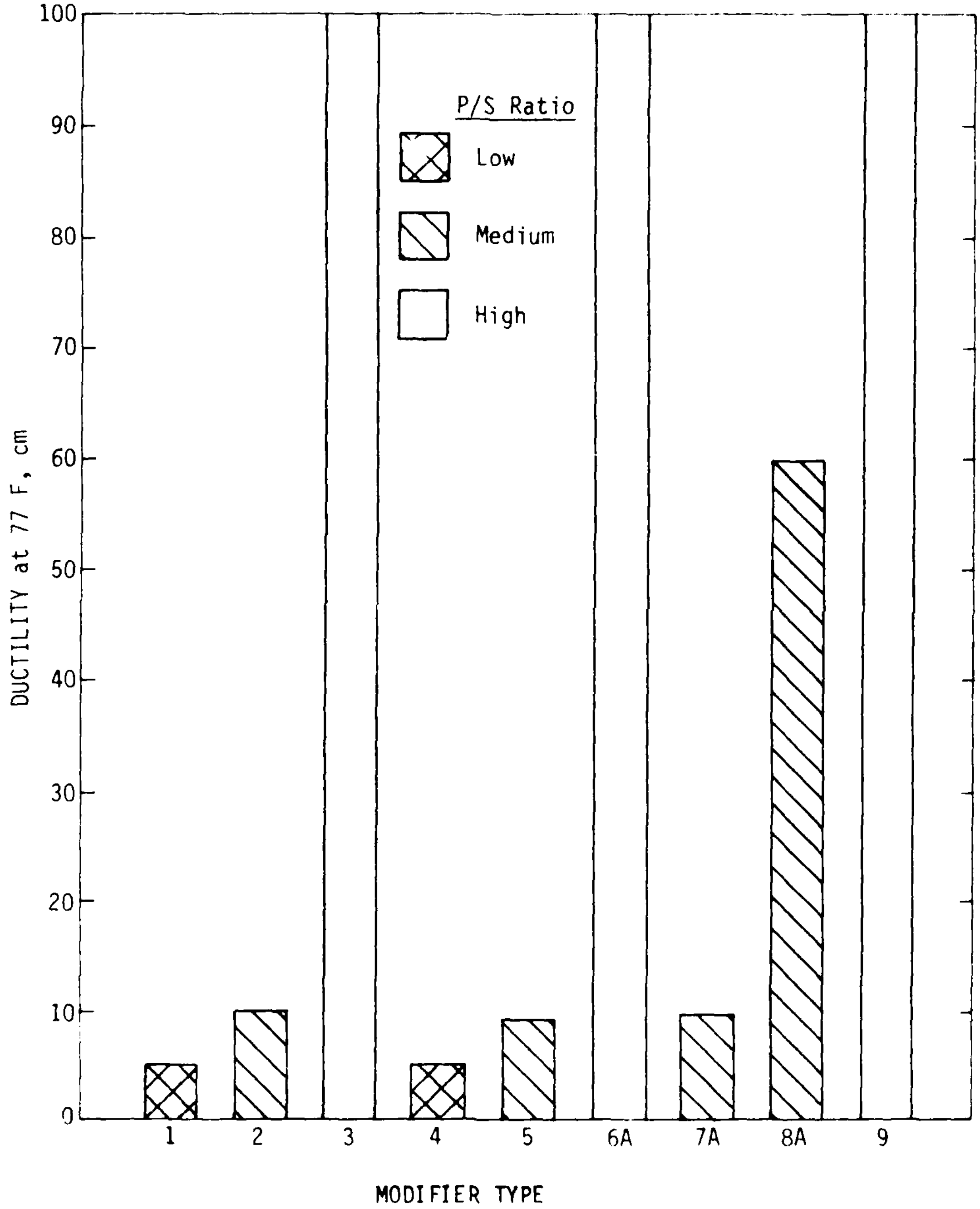

Figure 17. Ductility of Pope AFB Blends After RTFO (Reference 81).

P/S ratio and percent generic aromatic content for blends in Pope AFB, Loring AFB, and Holloman AFB matrices. Ductility retention at 77°F for Pope AFB blends increases with increasing P/S ratio and increasing percent generic aromatic content. Similar trends were generally observed in Loring AFB and Holloman AFB matrices although the variation in these two matrices was not as dramatic as it was in Pope AFB matrix. This is probably because Loring AFB and Holloman AFB aged asphalts accommodated a wider range of modifiers than Pope AFB aged asphalt.

The ductility observations reported here were similarly observed in the NMERI analyses of published data on California coastal and valley asphalts. The results were more dramatic for California coastal asphalt than for California valley asphalt.

Aging Index

Aging index was observed to decrease with increasing P/S ratio of the modifier as summarized in Figure 18 (Reference 81). This trend was observed in all matrices conducted in this research. Figures C-2 and C-4 summarize the results for the Loring AFB and Holloman AFB matrices. These trends were similarly observed in the analyses conducted on California coastal and valley asphalts except the coordinate was N/P which is defined in Equation 3.

Aging index was observed to increase linearly as the sum of asphaltenes and saturates of the modifiers increased. This result is presented in Figure 19 (Reference 89).

Aging index was also observed to increase as the asphaltene peptizability increased or as the solvent power of the maltenes decreased. The results in this study further show that aging index decreases with increasing state of peptization as will be discussed it the section on correlations from compatibility test results.

Retained Penetration

Retained penetration at 39.2°F and 77°F after RTFO conditioning tended to increase with increasing P/S ratio as shown in Figures 20 and 21 in the Pope AFB matrix.

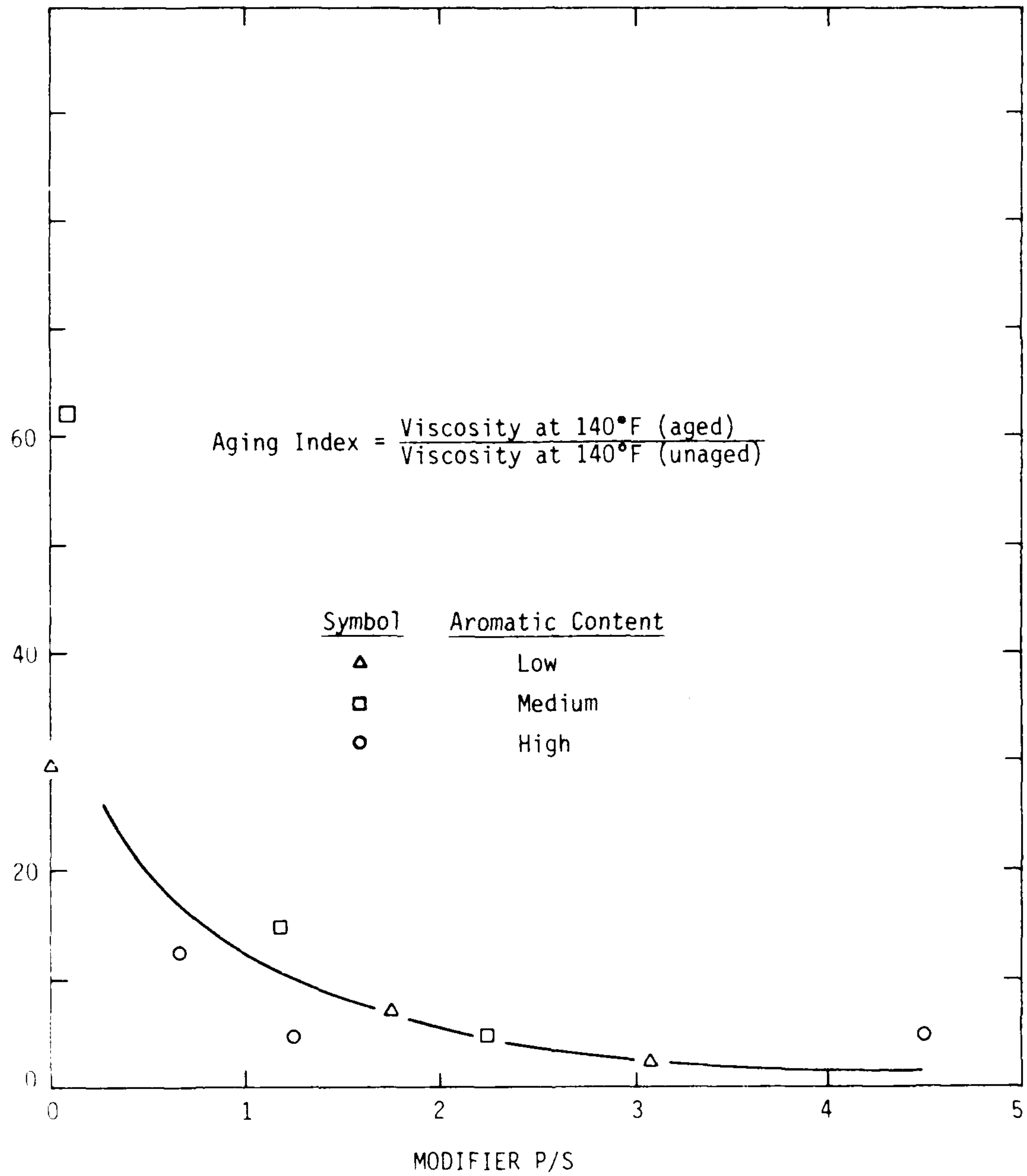

Figure 18. Effect of Modifier P/S on Aging Index of Pope AFB Blends (Reference 81).

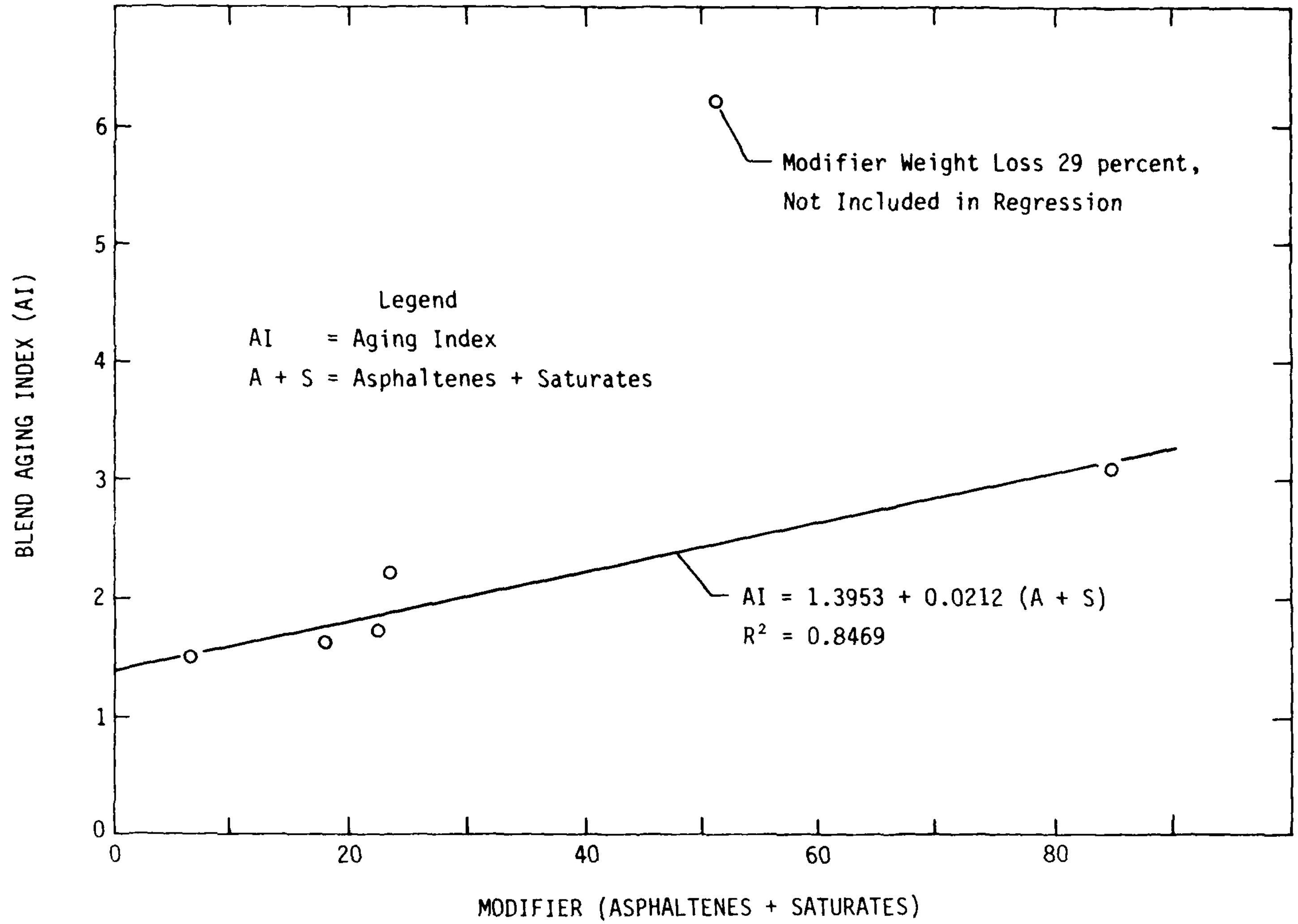

Figure 19. Blend-Aging Index versus Modifier (Asphaltenes + Saturates) (Loring AFB) (Reference 89).

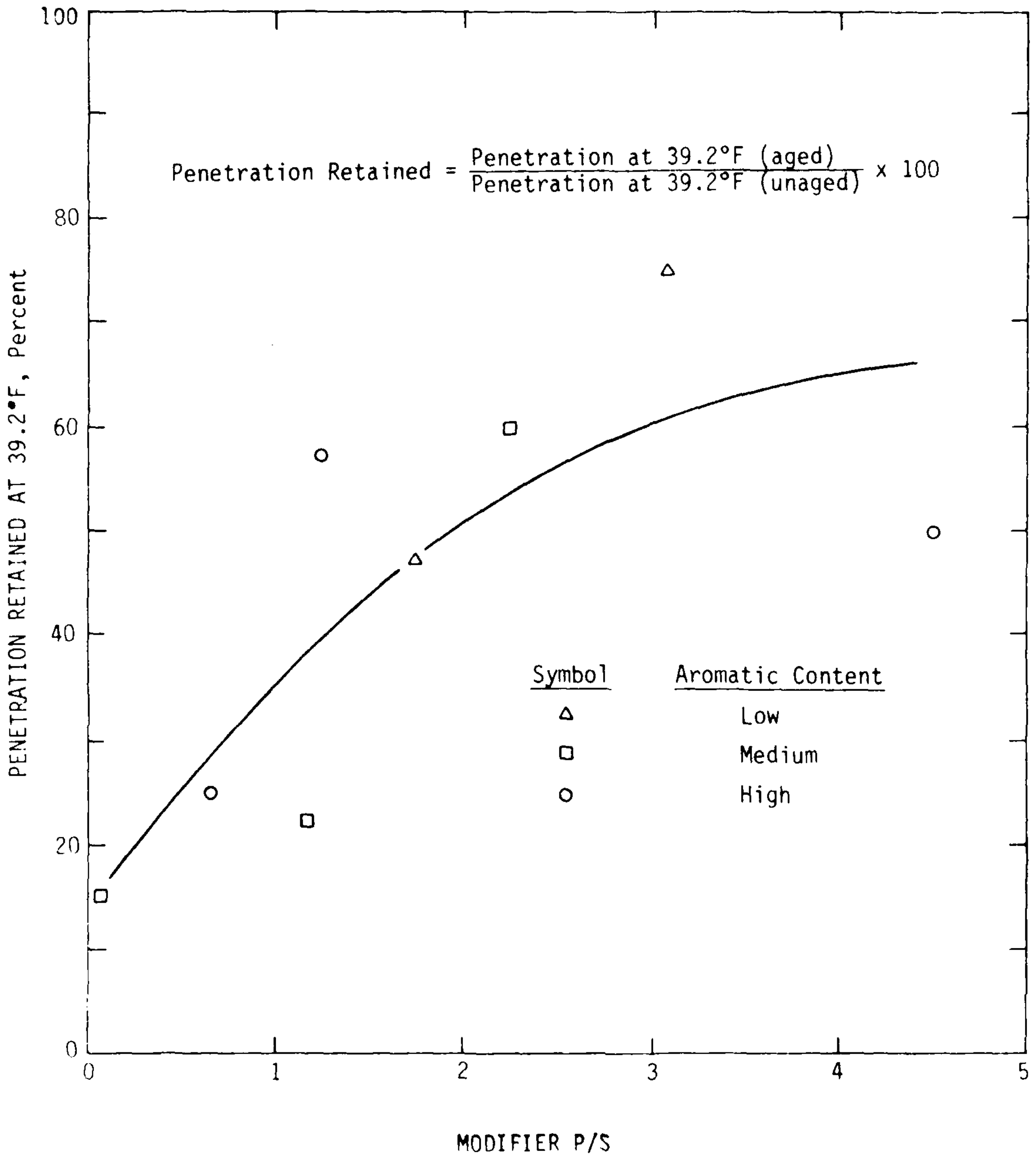

Figure 20. Effect of Modifier P/S on Percent Penetration Retained at 39.2 After RTFO (Reference 81) (Pope AFB).

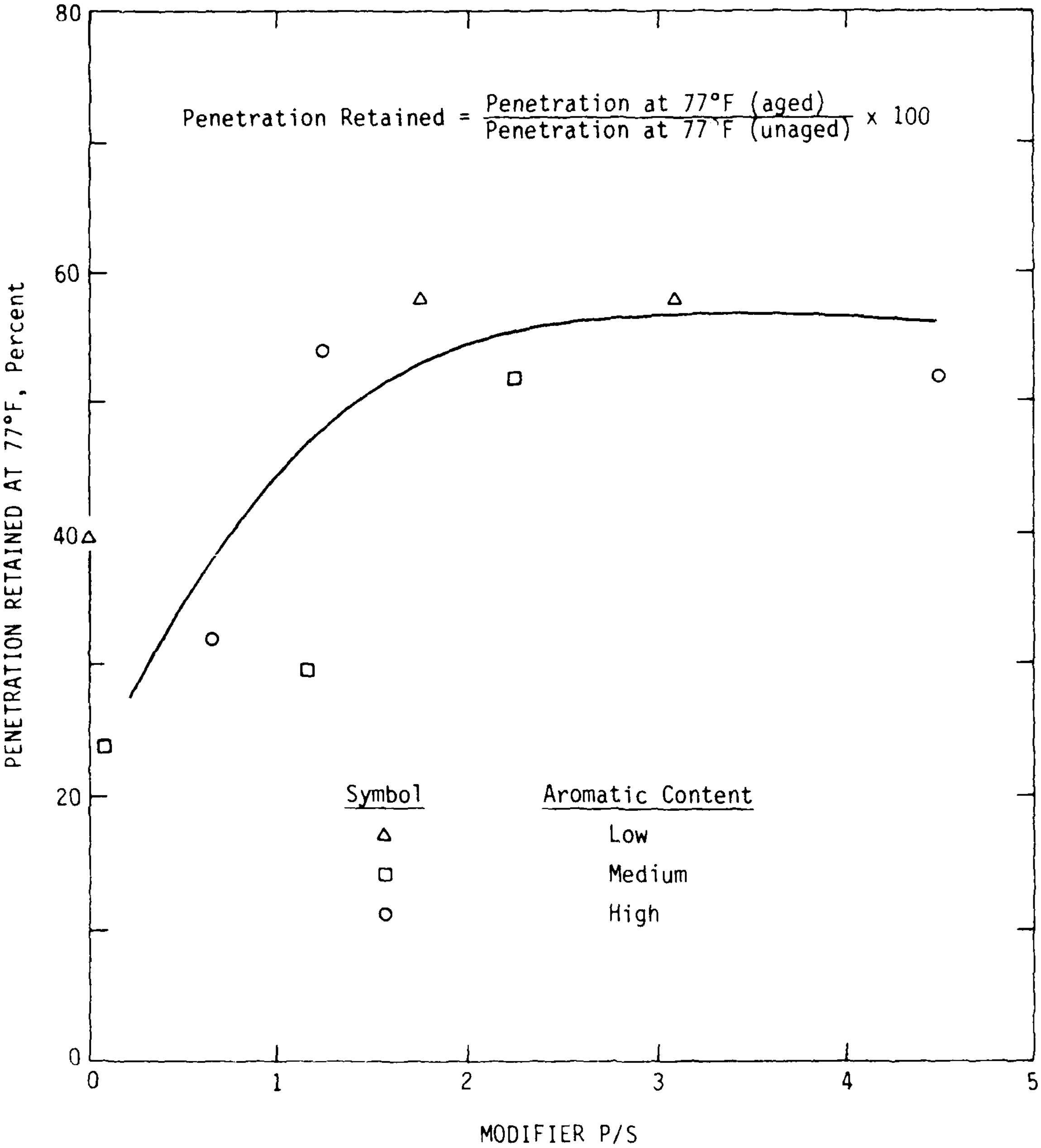

Figure 21. Effect of Modifier P/S on Percent Penetration Retained at 77°F After RTFO (Reference 81) (Pope AFB).

the relative solvent power of the maltenes. The addition of paraffins only makes the situation worse.

Kolbanovskaya (Reference 101) has shown that the maltene phase of some asphalts will tolerate more asphaltenes than others prior to rapid increase in viscosity. This is shown diagrammatically in Figure 30.

Hillyer et al. (Reference 94) observed that as the solvent power of the solvent in a concentrated polymer solution becomes weaker, the relative viscosity of the solution drastically increases. This is the opposite of what is found in dilute solutions. The cause is a flocculation of the polymer (or in the case of asphalt, asphaltenes), which causes the marked increase in viscosity. Consider two asphalts, one in which the asphaltenes were well-dispersed (A) while in the other, the parrafin content is high, and the solvent power is reduced (B), see Figure 31. Before oxidation, they both have the same viscosity. Assume that they each undergo the same amount of oxidation, or increase in polarity. The viscosity of A changes very little (i.e., like California valley asphalt) and the maltene fraction has sufficient solvent power to handle the increase in polarity without difficulty. The case of asphalt B is different. The increase in polarity causes a very rapid increase in viscosity, much more than can be explained by oxidation alone. The increased polarity destabilizes the solution of asphaltenes in the maltenes, causing flocculation of the asphaltenes and an increase in the viscosity.

With the Loring AFB asphalt and, to a limited extent, the Holloman AFB asphalt, the detrimental effect of the paraffinic oils were much less dramatic. In other words, the Pope AFB asphalt, had a very low tolerance for paraffinic oils while the Loring AFB asphalt and Holloman AFB asphalt had high tolerance. This is quite consistent with the mechanism described above, and shown in Figure 31. This also suggests that the specification criteria for the recycling agents in a particular project should vary, depending upon the nature of the asphalt.

Aphalts which appear to be sensitive to paraffinics and to viscosity increase with aging also tend to be high in asphaltenes. This was also found in this study. The asphalt from Pope AFB contained 43.6 percent asphaltenes

SMS. MBD-2B2 showed a similar trend although the SMS region was increased more than desired. While the physical properties of MBD-3B2 were considered good, several other blends were as good or better with respect to aging index, retained penetration and ductility.

Effect of Recycling Agent Composition on Viscosity and Aging Index

Blends of Pope AFB asphalt and paraffinic recycling agents had high viscosities and aging indices after oxidation in the RTFC oven. This appears to go against conventional wisdom. Paraffinic oils are more resistant to oxidation than are aromatic oils; thus one would expect that softening asphalt with a paraffinic oil should improve its aging characteristics.

Rostler (Reference 97) has stated "High content of liquid paraffins gives asphalts a high durability, provided the amount is not so high as to give the asphalt a cheesy or putty-like consistency." His concept is based upon the fact that the paraffin portion of asphalt is much more resistant to oxidation than are the other portions. Experience has demonstrated, however, that in spite of their resistance to oxidation, the addition of paraffins reduces the performance of asphalt. White et al. (Reference 98) have demonstrated that the most internally stable asphalts are those in which the nitrogen based (polar compounds) and reactive aromatics are increased, and the paraffins (saturates) are decreased. Kemp (Reference 99) has shown that the Heithaus approach correlates much better to field performance than does the Rostler approach. Anderson et al. (Reference 100) have demonstrated that the Rostler approach of maximizing paraffins leads to an increase in pavement cracking, while increasing the polar compounds with respect to paraffins leads to a decrease in pavement cracking.

Apparently something other than oxidation is involved in the marked increase in "aging" (with aging being defined as a viscosity increase) of blends of asphalt with paraffinic oils. Rostler's approach should be correct if no asphaltenes are present. In the presence of asphaltenes, his approach is incomplete because asphaltenes are not soluble in paraffins and increasing the paraffinic content reduces solvent power of the maltenes for the asphaltenes. If enough paraffins are added, the asphaltenes would be excepted to precipitate, which is the condition described by Rostler as being "cheesy." Oxidation of an asphalt makes the asphaltenes more polar from the formation of ketones and carboxylic acid anhydrates (References 67 and 69) which reduces

Clay-Gel Compositional Analysis

It has become obvious throughout this report that the emphasis on Clay-Gel analysis is not unwarranted. Besides the fact that the original matrices were constructed using Clay-Gel data, i.e., polar-to-saturate ratio and percent generic aromatic content, the correlations observed between P/S and percent aromatics have been enumerated previously in the subsections that deal with physical data. The P/S ratio has been particularly significant at low and medium aromatic content with respect to ductility, retained penetration and aging index and especially in the Pope AFB matrix. As the aromatic content increases, the P/S ratio becomes less of an influence on these parameters. The Loring AFB and Holloman AFB matrices show the same trends, but the differences between blends are not as dramatic as with the Pope AFB matrix.

The underlying section will present correlations observed from the High-Pressure Gel Permeation Chromatography test results.

HP-GPC

Direct correlations between HP-GPC data and physical data are difficult because of the form in which the HP-GPC data is presented. However, trends can be seen that follow the same trends found in the physical tests. In the previous section on results, it was stated that for the Pope AFB matrix, MBD-3 modifier was the "best bet" to restore the aged binder. This choice was made, based upon HP-GPC data alone, with no physical data information. When the HP-GPC analyses were run on the blends themselves, MBD-31 reduced the LMS region the greatest amount, and also increased the MMS and SMS regions. Upon RTFO aging, MBD-31 had the smallest increase in LMS material except for MBD-51. However, MBD-51 did not reduce the LMS region in the original blend by a substantial amount. This information also correlates very well with physical data. MBD-31 had the lowest aging index, the ductility remained over 100 cm and highest-percent penetration retained after RTFO at both 39.2°F and 77°F. In the Loring AFB matrix, MBD-3B and MBD-6B were likely candidates in restoring the aged binder, with MBD-3B the most likely choice because it would increase the SMS region the smallest amount while still reducing the LMS material. After HP-GPC data were collected from the Loring AFB blends, MBD-3B2 showed a significant reduction in LMS material, an increase in both MMS and

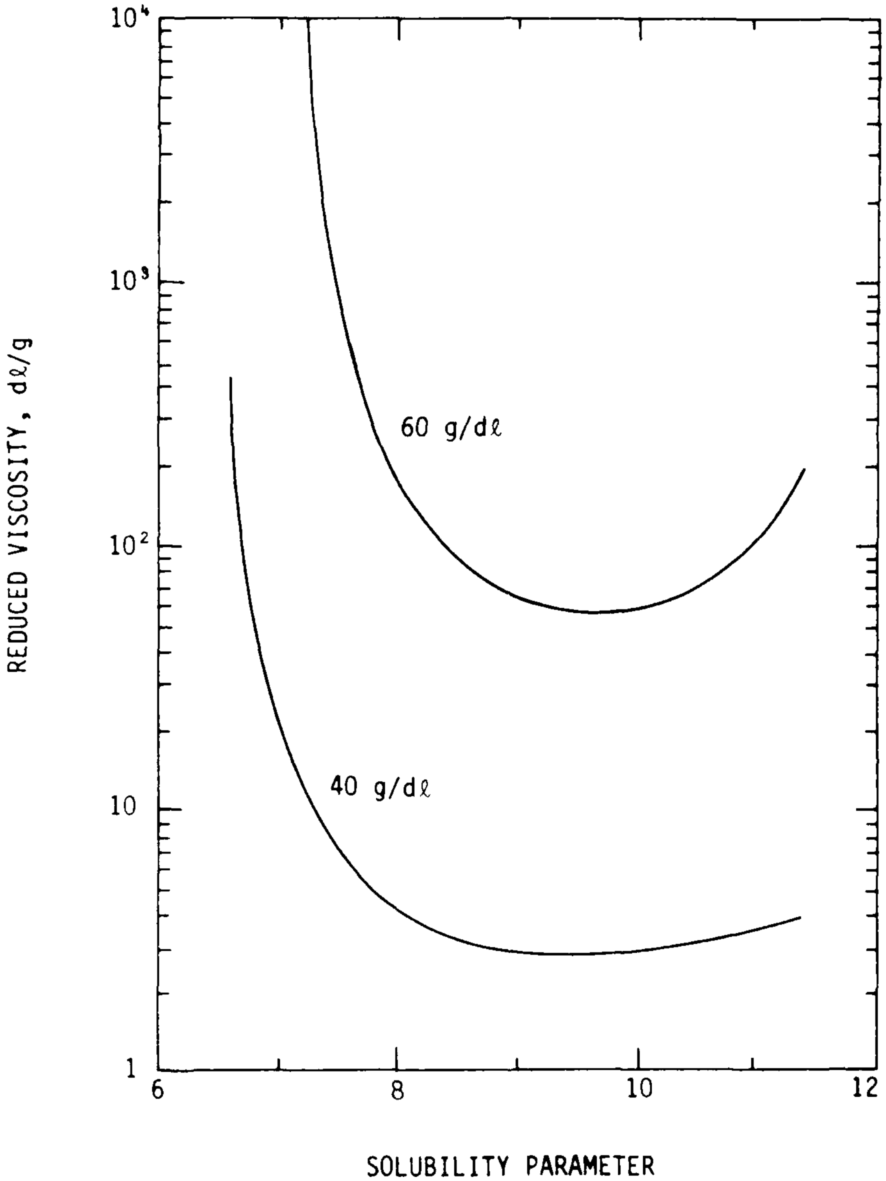

Figure 29. Reduced Viscosities of Beckosol 7 as Predicted Using Model Coefficients and a Range of Solubility Parameters (Reference 94).

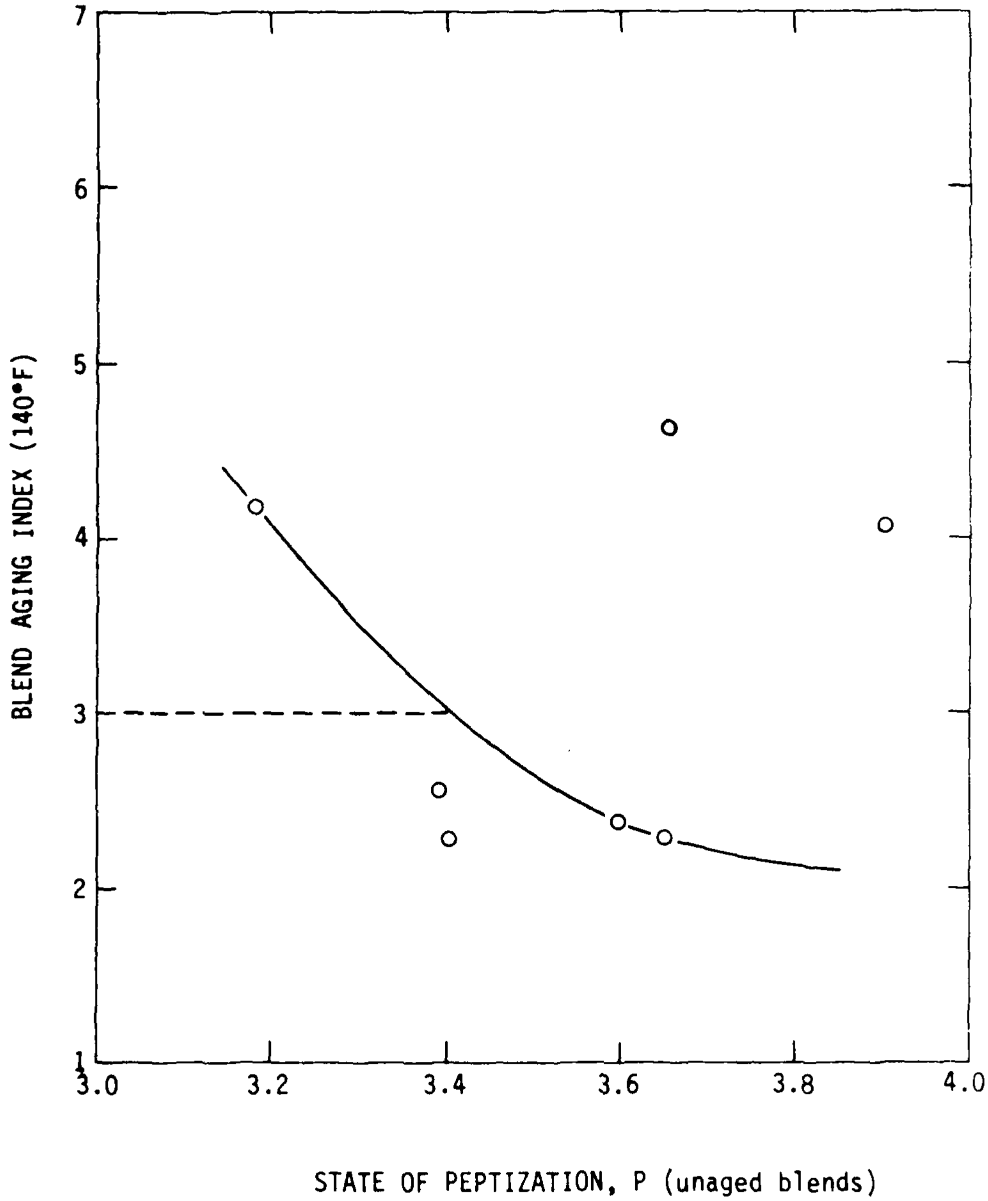

Figure 28. Blend-Aging Index (140°F) versus State of Peptization (Unaged Holloman AFB Blends).

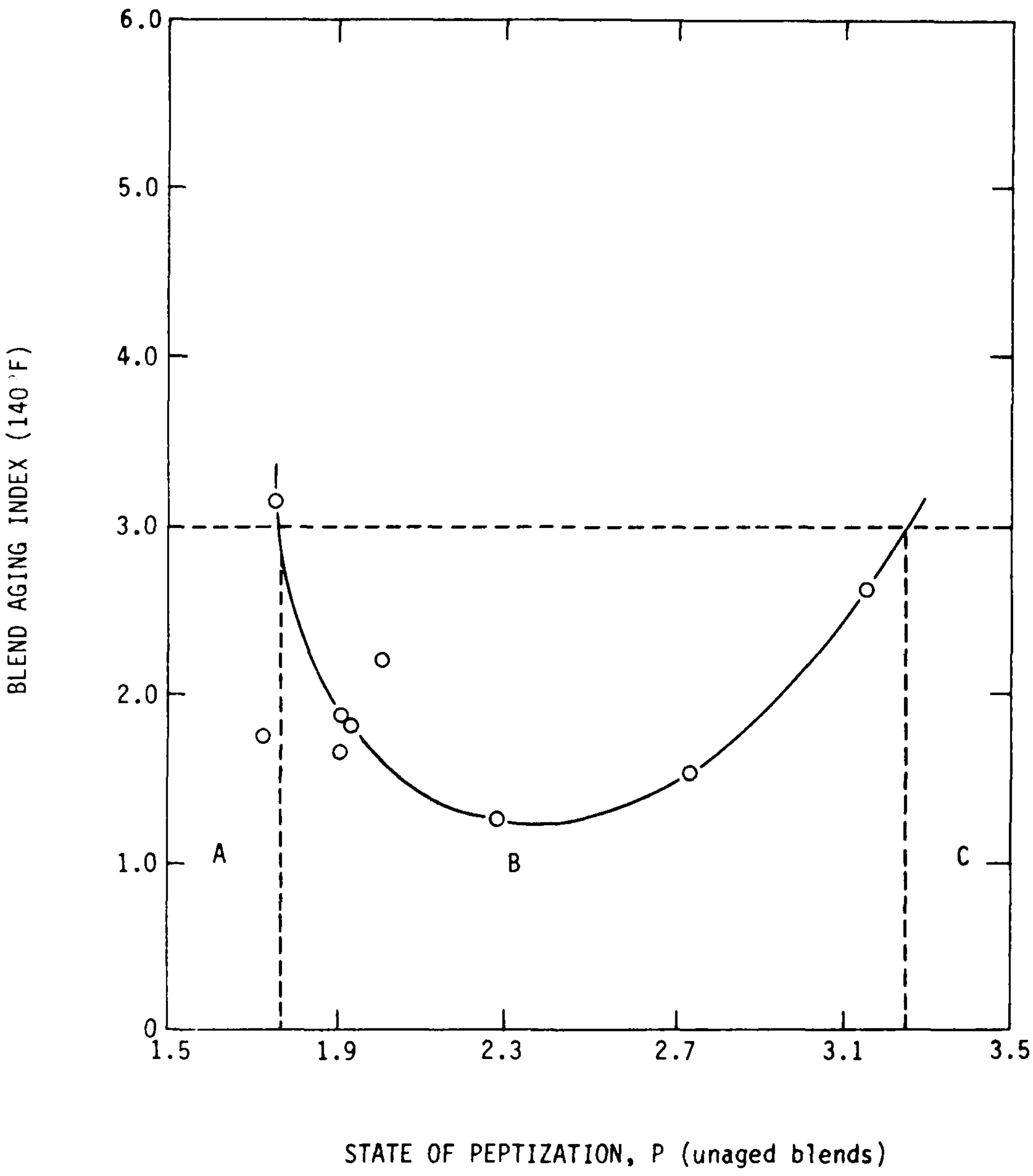

Figure 27. Blend Aging Index versus State of Peptization (Unaged Loring AFB Blends).

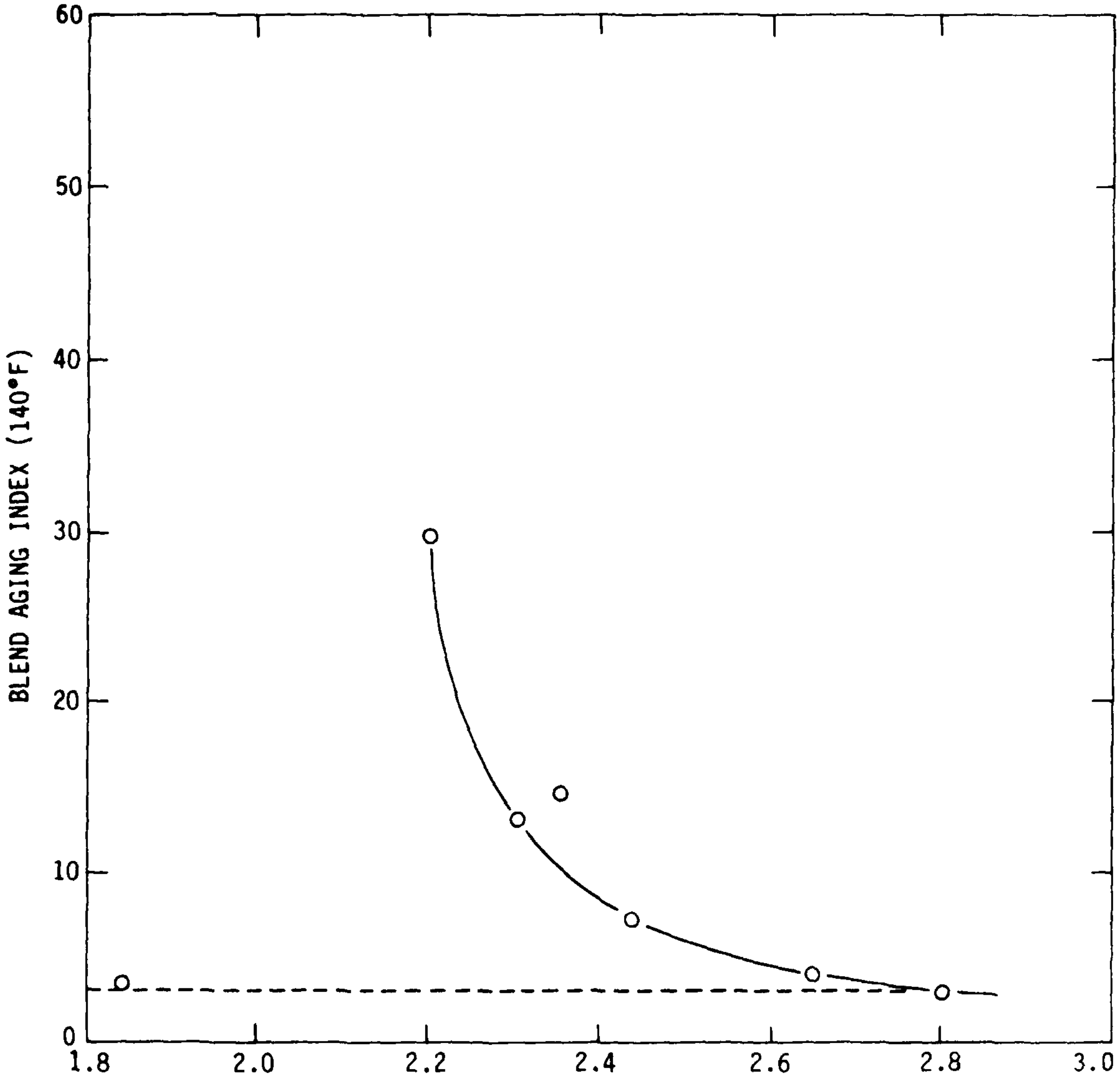

Figure 26. Blend Aging Index (140 F) versus State of Peptization (Unaged Pope AFB Blends.

Figures 26, 27, and 28. The shapes of these relationships are typical of the results expressed by Hillyer, et al. (Reference 94) relating log-reduced viscosity versus the solubility parameter of polymeric materials. These results are summarized in Figure 29.

The shape of the results in Figure 28 can be used to propose compatible and incompatible regions from solubility test results obtained in this study. The proposal is that if an Aging Index of 3 is preferred for a recycled blend, then a horizontal line can be drawn through this valve, say on Figure 28 for Loring AFB. This line will intersect the aging index versus state of peptization relationship at two points. The projections of these points to the horizontal axis divides the curve into regions A, B, and C, respectively. Regions A and C are characteristic of increasing viscosities of blends and thus are termed incompatible regions. Region B is considered to be representative of compatible blends. This proposal implies that modifiers which lead to blend viscosities of aging indices in region B would be most preferred on the basis of compatibility. This proposal is still tentative and remains to be verified by additional research effort. Additional correlations have been attempted between the asphaltene peptizability of the unaged blend and the modifier P/S ratio. This relationship yielded the following tentative formulations:

$$P_a = 0.299 + 0.039\left(\frac{P}{S}\right)_{\text{modifier}} \tag{10}$$

with a coefficient of correlation R = 0.728 for the Pope AFB matrix and

$$P_a = 0.151 + 0.109\left(\frac{P}{S}\right)_{\text{modifier}} \tag{11}$$

with a coefficient of correlation of R = 0.913 for the Loring AFB matrix.

The relationship for the Holloman AFB matrix has not yet been determined.

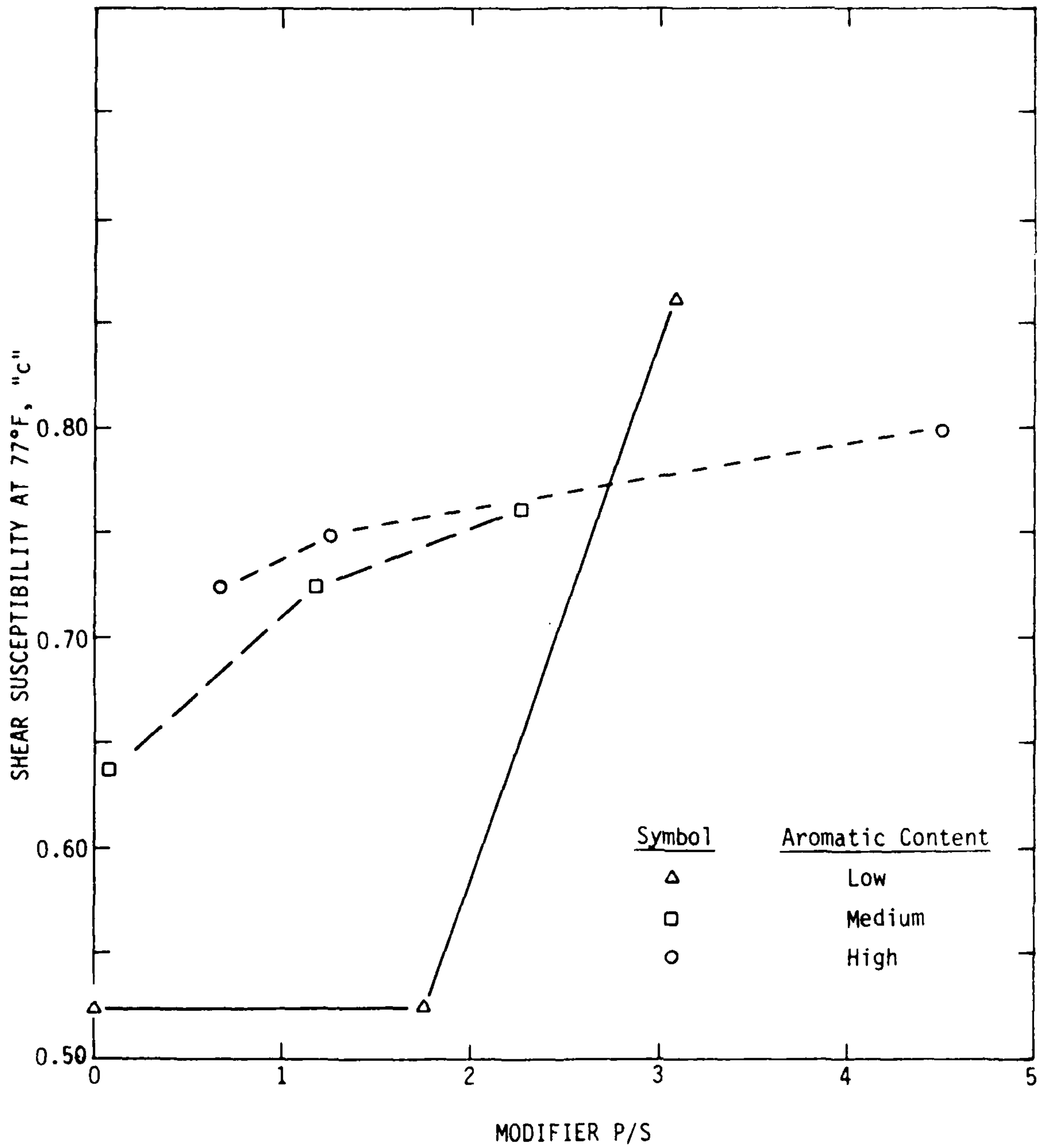

Figure 25. Effect of Modifier P/S on Shear Susceptibility at 77°F (Reference 81) (Pope AFB).

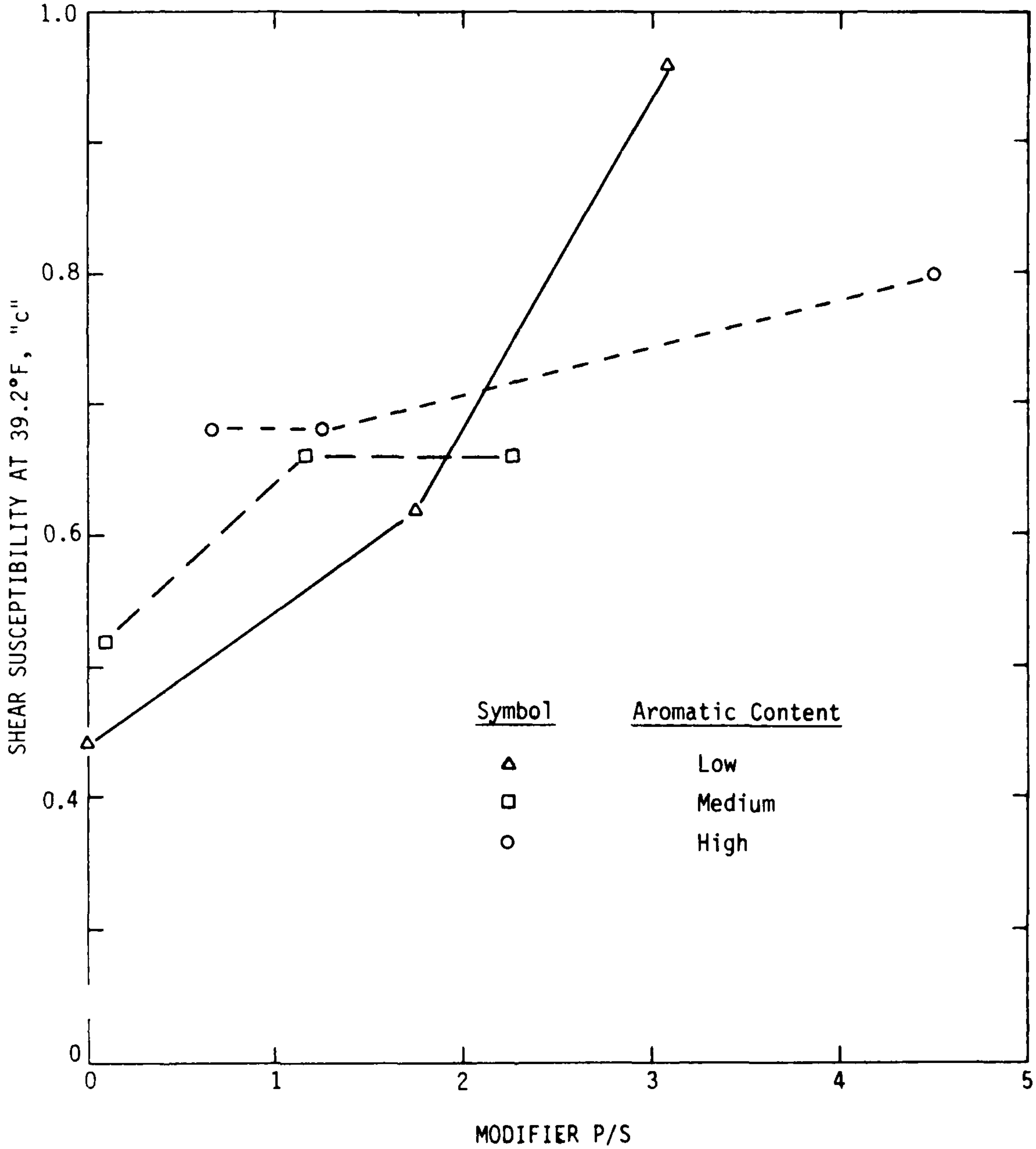

Figure 24. Effect of Modifier P/S of Shear Susceptibility at 39.2°F (Reference 81) (Pope AFB).

Shear Susceptibility

The variation of shear susceptibility on changing P/S ratio of modifiers shown by the Pope AFB matrix is summarized in Figures 24 and 25 (Reference 81) at 77°F and 39.2°F. In these figures, shear susceptibility generally decreases with increasing P/S at any level of percent generic aromatic content. This variation seems to be masked by increasing levels of percent generic aromatic content.

Similar observations were generally noted, as summarized in Figures C-9 through C-12, for the Loring AFB and Holloman AFB matrices.

Resilient Modulus

The resilient moduli of recycled mixes generally decreased with increasing P/S ratio for the medium- and high-percent generic aromatic contents upon continued oven aging. This trend was maintained generally throughout the aging period as shown in Figure 8. For the low-percent aromatic content, the modulus increased with increasing P/S ratio. The results summarized in Figure 8 pertain to the Pope AFB matrix. The results from the Loring AFB matrix are summarized in Figure 9.

Two controls in each matrix were manufactured with aggregates from the Pope AFB RAP, Loring AFB RAP, and a local source. The mixes made with the aggregates from the parent RAP tended to be softer than the mixes made with the fresh aggregate throughout the entire aging period. The difference in stiffness is probably more from the interlock characteristics of the aggregates. However, the observed differences can also be attributed to the asphalt-aggregate chemical interaction effects.

Correlations from Compatibility Test Results

From the study of three aged asphalts, the observable trends are that aging index decreases with increasing asphaltene peptizability (P_a) and the asphaltene state of peptization (P). The relationships for aging index versus asphaltene state of peptization for the three matrices are summarized in

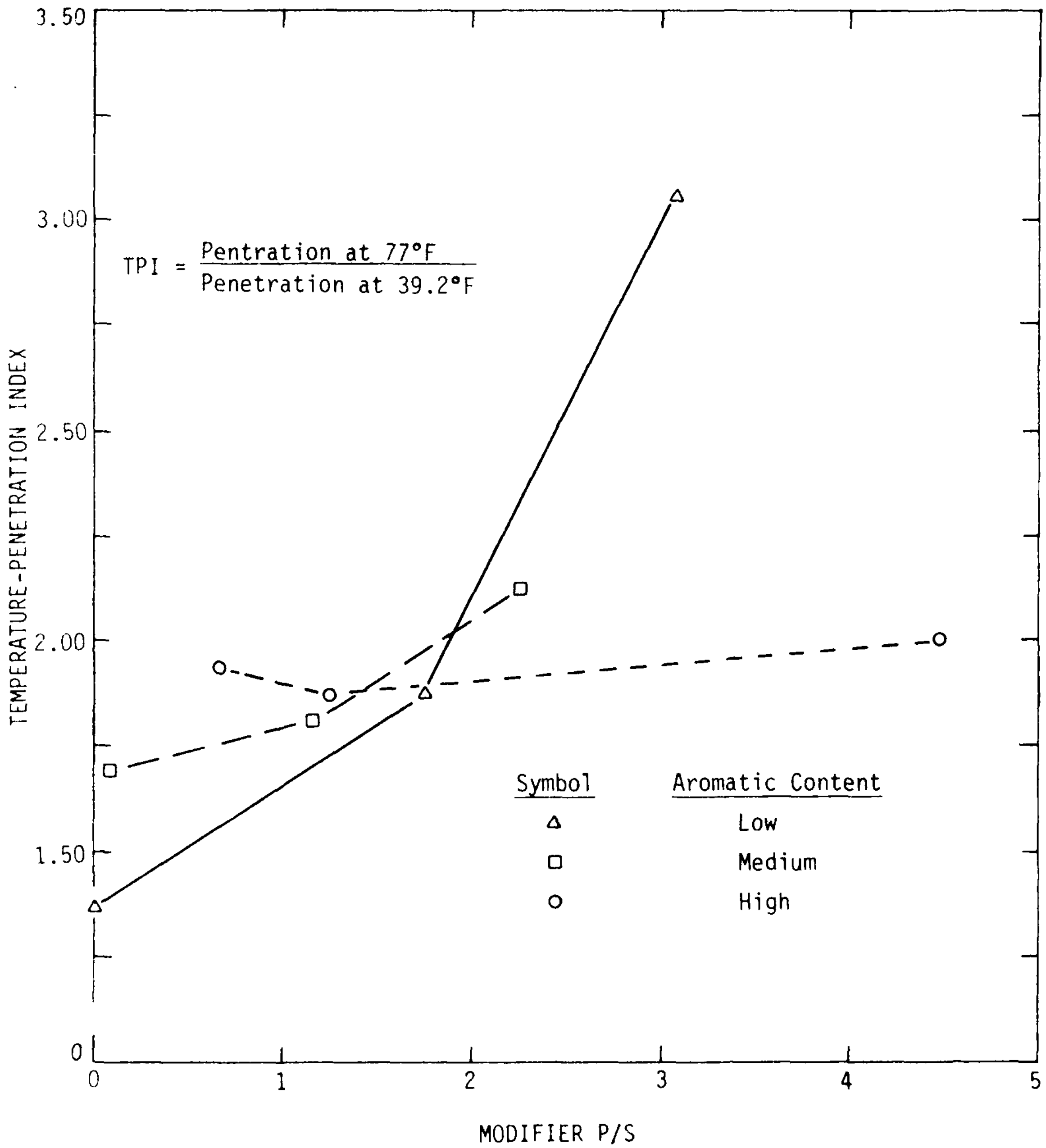

Figure 23. Effect of Modifier P/S on Temperature-Penetration Index (Reference 81) (Pope AFB).

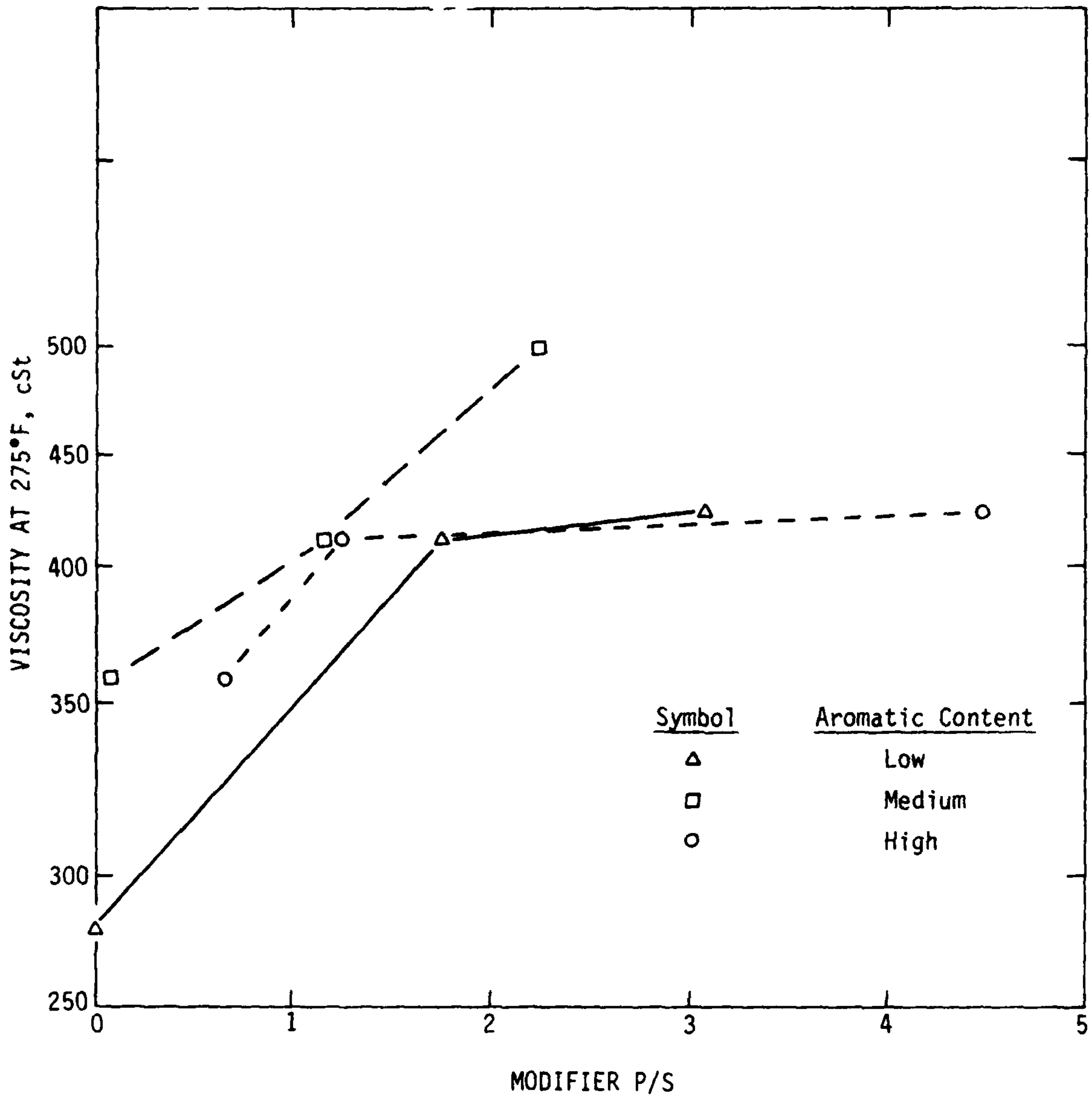

Figure 22. Effect of Modifier P/S of Viscosity at 275°F (Reference 81) (Pope AFB).

In the Loring AFB matrix this variable hardly showed any predictable trends. However, at 77°F, retained penetration decreased with increasing P/S ratio at the low percent generic aromatic content.

Viscosity

Figure 22 (Reference 81) presents the effects of changing P/S ratio on high-temperature viscosity (275°F) of the blends. High-temperature viscosity increases with increasing P/S ratio in Pope AFB blends. In Loring AFB blends, high-temperature viscosity decreased with increasing P/S ratio in either category of percent generic aromatic content as summarized in Figure C-5 in Appendix C. The results on the third field-aged asphalt generally indicated that high-temperature viscosity increased with increasing P/S ratio in the medium percent generic aromatic content. The results further showed that increasing percent generic aromatic content masked the effects of increasing P/S ratio. Mixed results were observed in the low-percent generic aromatic content category. The results are summarized in Appendix Figure C-6.

Temperature-Penetration Index (TPI)

This index was developed in this study as the ratio of penetration at 77°F to penetration at 39.2°F. The higher the value of TPI, the higher the temperature susceptibility. Figure 23 (Reference 81) summarizes the findings for the Pope AFB matrix. Figure 23 shows that blends made with modifiers of low-percent generic aromatic content show increasing low-temperature susceptibility with increasing P/S ratio. The changes in this variable, TPI, become minimal as the percent generic aromatic content increases. The results for the Loring AFB matrix are presented in Figure C-7. These results indicate increasing low-temperature susceptibility with increasing percent generic aromatic content. However, the variation is smaller as the percent generic aromatic content increases. The variation in the low-percent aromatic content is similar to the observation in the Pope AFB matrix. Finally in Holloman AFB blends, the results summarized in Figure C-8 indicate that low-temperature susceptibility is independent of percent generic aromatic content as the P/S ratio varies.

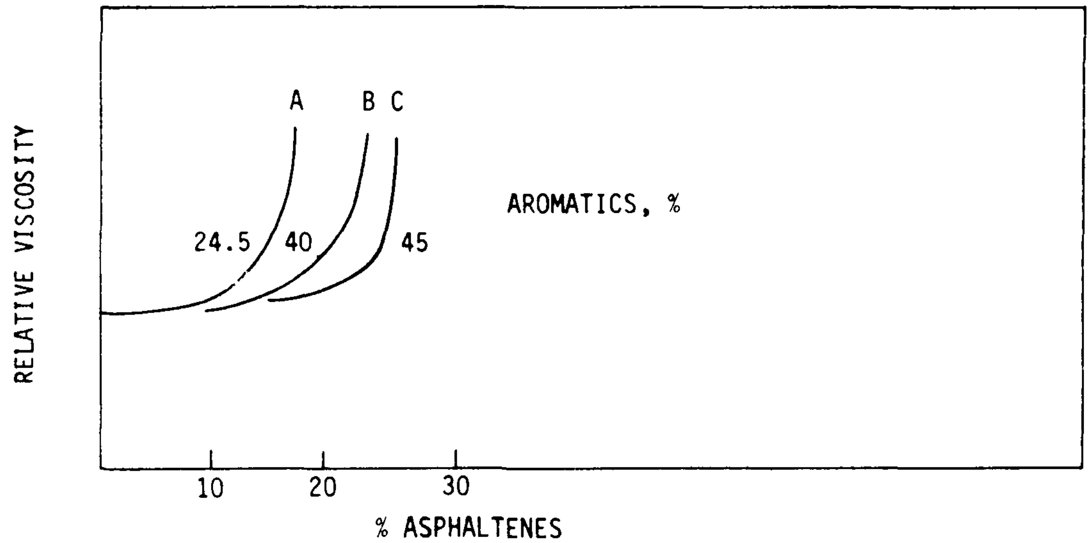

Figure 30. Effect of Asphaltenes on Asphalt Viscosity.

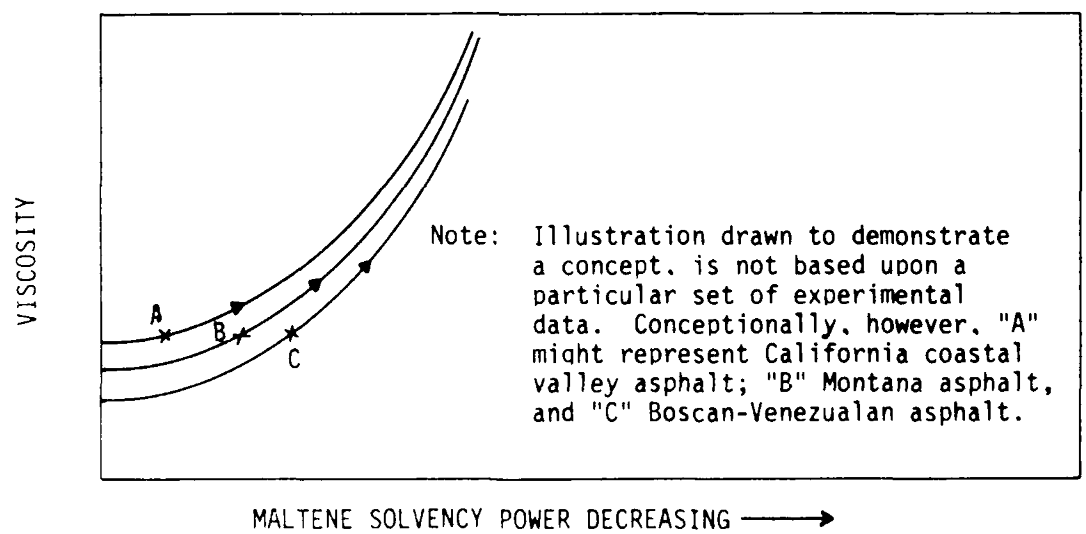

Figure 31. Illustration of the Effect of Maltene Solvent Power on Resistance to Age Hardening.

and was very sensitive to paraffinic recycling agents while the asphalt from Loring AFB contained only 27.6 percent asphaltenes and was much more tolerant to paraffinics. The effect of asphaltenes on the ability of an asphalt to tolerate paraffinic oils was the basis for the recommended specification criteria that the sum of the saturates and asphaltenes from the Clay-Gel analysis of a recycling agent should not exceed 30 percent.

SECTION VI
CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The overall objective in this effort was to develop a procedure by which a standard laboratory can define appropriate modifiers to recycle old paving-grade asphalt in hot central plant recycling operations. The approach to this effort initially involved identifying a wide variety of physical and chemical methods. The physical methods which were identified are contained in ASTM Volume 04.03 (Reference 79) and Schweyer viscosity (Reference 78). These methods are conventionally used by some affiliates of the DOT, asphalt research institutions, and oil companies. The chemical methods which were identified included Clay-Gel (ASTM D-2007), Heithaus/Waxman solubility test (compatibility), High-Pressure Gel Permeation Chromatography (HP-GPC), and on a limited basis Elemental Analysis, Infrared Spectroscopy (IR), Nuclear Magnetic Resonance (NMR), and Electron Paramagnetic Resonance (EPR). The above methods were applied to field-aged binders, modifiers, unaged blends, RTFO blends, and recovered oven-aged recycled binders.

From analyses of modifiers by a modified Clay-Gel procedure, the generic chemical information was used to develop two chemical parameters or test variables which are polar/saturate ratio and percent generic aromatic content. Nusser et al. (Reference 91) addressed mass balance considerations in the generic composition analyses involving all the asphaltic materials tested in this study. Such considerations enunciated by Nusser et al. led to improved recoveries, repeatability and confidence level in the composition information.

Based on the Clay-Gel data, three three-by-three test matrices were constructed. The blends were prepared and analyses, both chemical and physical began. The testing for the three matrices is complete and results and correlations have been reported. The observations made in this report are subject to further verification with the continuation of this research effort using more aged pavements for laboratory study and the beginning of field trials. The following conclusions are based on the test data and correlations made:

1. As the P/S ratio of the modifier increased and the aromatic content was low or medium, the low-temperature susceptibility generally increased.

2. As the P/S ratio of the modifier increased, the blends exhibited less shear susceptibility at 39.2°F and 77°F.

3. For Pope AFB blends, the blend viscosity at 275°F increased with increasing P/S ratio. However, in Loring AFB blends, this trend did not hold true. In Holloman AFB blends, blend viscosity at 275°F increased with increasing P/S ratio expecially in the medium percent generic aromatic content. Generally for all matrices increasing percent generic aromatic content masked the effects of increasing P/S ratio especially for P/S ratio greater than 1.0.

4. As the P/S ratio increased, the aging index of the blends decreased. This was generally true in the three matrices.

5. Ductility of the blends increased as the P/S ratio of the modifier increased. For the Pope AFB matrix with a target viscosity of 4000 poises, ductility tests were conducted at 77°F, and for the Loring AFB matrix, with a target viscosity of 500 poises, ductility tests were conducted at 60°F. Ductility tests for the Holloman AFB matrix with a target viscosity of 2000 poises were conducted at 60°F. This test was not very discriminatory for blends in the Holloman AFB matrix and the Loring AFB matrix at 77°F.

6. The penetration retained after RTFO of the blends increased with increased modifier P/S ratio in the Pope AFB matrix. This same trend was not well-defined in Loring AFB matrix. In the Holloman AFB matrix, a fair relationship exists. The correlations are more defined at 77°F.

7. Modifiers are not compositionally additive to the aged asphalt fractions. In fact, modifiers redisperse the asphaltenes and the calculated percentages of each Clay-Gel fraction are not the same as the actual values.

8. Upon RTFO aging, the polar fraction decreased and the asphaltene fraction increased.

9. As the sum of the asphaltene and saturate fractions in a modifier increased, the aging index of the blend increased.

10. Compatibility between the modifiers and the aged binders can be determined by the Heithaus/Waxman procedure. Aging index of the blend most probably defines the compatibility relationship, when plotted against asphaltene state of peptization.

11. HP-GPC can be used to provide more information on the compatibility of modifiers and aged binders. This information is evidenced by a reduction in the LMS region of the blends.

12. Mixtures prepared from recycled blends age at a slower rate than virgin mixtures. The viscosities at 140°F of recovered binders from oven-aged mixtures generally decreased with increasing P/S ratio in each group of percent generic aromatic content.

13. This study has indicated so far that there is no universal modifier for every aged binder. That is, in general, the effects of each modifier are aged asphalt-specific in general. In addition some aged asphalts are more recyclable than others as the cases for the Pope AFB matrix versus the Loring AFB matrix and California coastal asphalt versus California valley asphalt exemplify.

14. Physical and chemical properties are necessary for better selection or definition of a modifier-aged asphalt-compatible relationship.

15. The higher the asphaltene peptizability (P_a), the lower the peptizing power (P_0) of the maltenes required to keep the asphaltenes dispersed.

16. Using the limited infrared analyses, modifiers appear to inhibit formation of oxidation products. The dispersive effects of modifiers for oxidation products may be measured by infrared analysis.

It is recognized that these conclusions are based on only three aged pavements and 14 modifiers. Therefore, they are subject to further verification using additional aged pavements and modifiers. Based on these observations and conclusions, a tentative specification for choosing a modifier for a recycling project has been designed and is the subject for the following subsection.

Tentative Modifier Selection Specification

The effort to date has enabled the formulation of the following tentative modifier selection specification for hot central plant recycling operations. This specification is considered tentative because of the limited data base and lack of a field trial verification. In the case of the former, additional laboratory effort is continuing with more field-aged asphalts and a variety of modifiers. This specification is developed using petroleum-derived products or modifiers. The tentative specification is presented in Table 34, along with references to efforts of other organizations, namely the American

TABLE 34. TENTATIVE SPECIFICATION FOR MODIFIER SELECTION FOR HOT, CENTRAL PLANT RECYCLING OF ASPHALT PAVEMENTS

PROPERTY	VALUE	ASTM REFERENCE	OTHER REFERENCE	REMARKS
A. PHYSICAL				
1. Viscosity, 60°C (140° F), P	1.00 (min)	D-2170	West Coast User Producer Group	ASTM subcommittee D04.37 recently adopted a 0.50-1.50 Poises range (Dec. 1983)
2. Viscosity, 100°C (212° F), cSt	15.00 (min)			
3. Flash Point COC, °F	425 (min)	D-92		At December 1983 meeting ASTM subcommittee D04.37 raised Flash Point from 400 to 425°F.
4. Viscosity Ratio From Aging (RTFO)	3.0 (max)	D-2872 D-2170	Chevron Research Company	Evaluated at 140°F
5. Weight Loss (RTFO) percent, 325°F for 85 min	1.0 (max)	D2872	ASTM subcommittee D04-37 meeting, June, 1984. Proposed 3-4 percent (maximum)	
B. CHEMICAL				
Composition Analysis:		Clay-Gel ASTM D-2007	NMERI modifications applicable (See Appendix A)	
1. (Saturates plus asphaltenes) by weight percent	30 (max)			The West Coast User Producer Group, Arizona DOT, Nevada DOT and California DOT call for 30 percent (max) saturate content. The ASTM subcommittee D04-37 has recently approved 25 percent (max) saturate content (June, 1984).
2. Polar/Saturate	Not less than 0.50 or twice the asphaltene fraction			The West Coast User Producer Group recommends minimum N/P = 0.50 (obtained by Rostler method).
C. COMPATIBILITY (solubility)				
The Heithaus procedure as modified at NMERI can be used as backup or support technique to verify the selection. Absolute numbers cannot be put in a specification because the values obtained are relative to the particular solvent system used. Consistency is absolutely essential for obtianing meaningful backup information. However, the use of aging index versus state of peptization relationship is proposed for fine tuning of modifier selection exercise.				

*These are ASTM test methods.

Society for Testing and Materials, ASTM; the West Coast User-Producer Group; and Chevron Research Company. This specification will be updated as soon as more information is obtained involving findings of the continuing effort as well as those efforts of other research institutions.

This specification is for binder rejuvenators and is intended to supplement, not supplant, existing ASTM specifications for binders. Final acceptance of any asphalt modifier depends on the blend it produces and the conformance of that blend (binder) to current specifications for asphalt pavements.

The authors made the following assumptions regarding the prospective use of this specification:

1. An economic decision has been made to recycle, using the hot central plant process.

2. The _in situ_ pavement materials have been thoroughly explored and characterized for gradation, binder content, variability of surface course layers, and depth of recycling as well as other parameters.

3. A construction procedure has been defined, along with quality control operations consistent with local practice. Typical examples are contained in References 95 and 96.

4. Existence of a well-defined contractor/USAF contract.

5. Preliminary decisions regarding mixture proportions, a set of candidate modifiers and the type of mix have been provisionally made.

RECOMMENDATIONS

The following list of recommendations are based on the work of previous published research efforts and the work performed in the present study.

1. A need exists to investigate more aged pavements and modifiers to establish precision limits of P/S ratio and percent generic aromatic content, as well as to verify the tentative specification.

2. The need exists to provide more effort towards defining polar functionality using spectroscopic techniques, and to compare polar functionality with compatibility analysis.

3. The temperature susceptibility of the blends at low- and high-temperature should be studied to further delineate the properties at those temperatures.

4. A need exists to study crude sources and climatic conditions to establish differences that might occur due to these variables. Water damage and freeze-thaw cycles can be very significant in the performance and durability of pavements.

5. A major need exists to investigate aggregate-binder interactions since this research effort involved only the study of the binder itself.

6. In the construction operation, a three-component system usually pertains in the process of recycling aged pavements. New virgin asphalt, the old-aged pavement, and a modifier are added to prepare the recycled blend. This three-component system needs to be studied to evaluate the effect of the virgin asphalt on the blend.

7. Increased research effort is required to verify modifier batch to batch effects on the properties of recycled blends and/or mixtures.

8. Ductility tests at various temperatures need to be investigated with respect to recycled mixtures. Such temperatures as 45°F and 32°F used in the states of Washington and Utah and other values prevalent in particular areas are good candidate values.

9. Finally, these laboratory investigations and findings need to be verified with field trials.

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PRECISION

At the New Mexico Engineering Research Institute, a variation of 5 percent between duplicate runs has been considered reasonable.

REMARKS

This method is not in the current ASTM specified methods of evaluating asphaltic materials.

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These graphical patterns of data presentation are typified in Figures 6, 7, and 8 in Section V. The results are also presented in a tabular form under the following parameters:

P_a = asphaltene peptiziblity

P_0 = peptizing power of the maltenes

P = state of peptization of an asphaltene dispersion

X_{min} = minimum volume of nonpolar solvent required to precipitate the least amount of asphaltenes.

$T_0 = X_{min}$

Cot ϕ = angle of inclination of the plot in item (3) above.

The mathematical relationships between the above parameters are described below:

$$P_a = 1 - FR_{max}$$

$$P_0 = FR_{max}\ (1 + X_{min})$$

$$P = 1 + X_{min}$$

$$\text{Cot}\ \phi = \frac{T - T_0}{S}$$

where

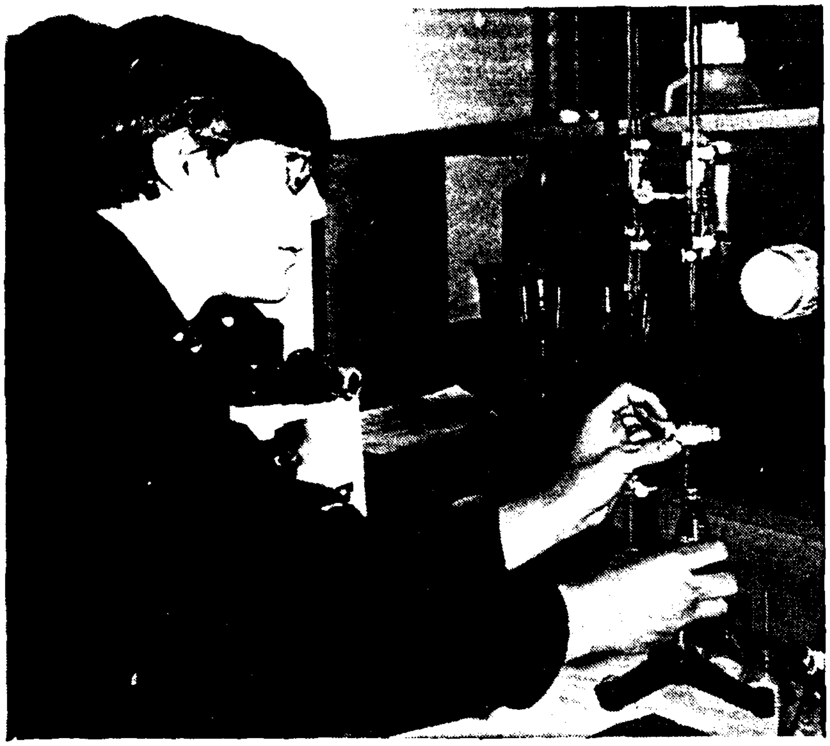
FR_{max} = ordinate intercept of the relationship FR versus DR^{-1}

T = volume of nonpolar solvent

S = volume of polar solvent

REPORT

This report should contain a summary of results on the parameters defined above. Graphical presentations are better indicators of changes in quality of materials than the absolute values. Thus, they should be presented. They also offer the testing personnel a self-check mechanism on the quality of workmanship.



(a) Solvent Titration.

(b) Flocculated Specimen.

Figure B-1. Compatibility Test Example.

2. Appliances - Microscope (with transmitted light features and movable stage

Magnetic stirrer

Magnetic stirring bars

OTHER EQUIPMENT

Filter papers

2 numbered stands

Clock or timer

One 35 mm camera

PROCEDURE

Weigh five 1.00 ± 0.05 gm samples in flasks. Dissolve the asphalt in a polar solvent (toluene) in volumes of 0.5, 1.0, 2.0, 4.0, and 6.0 ml. Duplicate tests are recommended for each test point. Titrate the nonpolar solvent into each solution of toluene-asphalt in increments of 1.0 ml or less to start with. After each addition of nonpolar solvent, shake or stir (magnetic stirrer) for 5 minutes. Then let the mixture set for another 5 minutes and observe for flocculation. If negative, then continue the process.

RESULTS

Flocculation of asphaltenes is the end point of interest. Figure B-1 shows some basic apparatus and a well-flocculated test. This photograph was taken at 160X. The results are presented graphically in the following format:

1. Flocculation Ratio (FR) versus Dilution Ratio (DR or X) where these terms were defined in the text as:

$$FR = \frac{\text{ml of polar solvent}}{\text{ml (polar + nonpolar) solvent}}$$

$$DR = \frac{\text{ml (polar + nonpolar) solvent}}{\text{grams of asphalt sample}}$$

2. Flocculation ratio versus inverse of dilution ratio and

3. ml of polar solvent (S) in ml/g versus ml on nonpolar solvent (Titrant) in ml/g.

APPENDIX B
COMPATIBILITY TEST

BACKGROUND

Background information to this test is to be found in earlier works by Heithaus (Reference 48), Skog (Reference 90), and Venable et al. (Reference 88) and personal communication from E. L. Dukartz. Venable et al. made modifications to the procedure which was reported in Reference 90. The New Mexico Engineering Research Institute made additional modifications as follows:

1. Sample size was reduced to 1.00 ± 0.05 gm and kept constant.

2. Five test points per each material in comparison to only four points in References 88 and 90.

3. Defined definite timing intervals betwen observations.

4. Microscopic magnification at 100-150X using transmitted light and finally,

5. Test temperature was 77 ± 5°F.

MATERIALS AND EQUIPMENT

Materials

1. These are aged asphalts, asphaltene-containing modifiers, blends and RTFO asphaltic samples.

2. Reagents include a polar solvent (e.g. Toluene) and nonpolar solvent (e.g. n-dodecane).

Equipment

1. Glassware - 125 to 250 ml flasks (Pyrex®).
   Two 50 ml burettes (for titration)
   Sampling glass rods
   Oil immersion slides with covers
   Dessicator

Figure A-3. Buchi Rotary Evaporation Setup.

Elimination of calcium chloride

The last modification to the Clay-Gel analysis technique involves the use of calcium chloride and a separatory funnel to rid the polar compound eluent of any water. This step was discarded because it was cumbersome, time-consuming, and because much material was lost in the filtering of the eluent. The polars stick to the filter paper and it becomes difficult to remove them and achieve mass balance. This step was eliminated by adding molecular sieves to the solvents before charging them to the columns.

Use of rotary evaporation

The use of a rotary evaporator for solvent evaporation has lessened the time factor significantly and made the solvent removal more efficient and complete. Figure A-3 illustrates the Buchi rotary evaporator setup.

This modified Clay-Gel analysis has been used on a variety of samples including virgin and aged asphalts, soft asphalts, recycling agents and blends (modifier plus aged asphalt) and the modifications have given satisfactory repeatability and mass balance. It is difficult to develop a method and solvent system that will work equally for aged asphalts as well as for light oil recycling agents, but the modifications generally work well for all of the systems under investigation.

Solvent system for polars

The original ASTM method calls for a maximum of 300 mls of a 50/50 mixture of benzene to acetone by volume to be used to strip the polar column. The benzene has been replaced by toluene in view of the carcinogenic classification of benzene. The clay column and eluent was still dark in color after addition of 300 mls of solvent. The percentages were altered to 30 percent toluene and 70 percent acetone and also the amount was increased to approximatly 1500 mls, or until the eluent is clear. The use of acetone has caused some concern by several experts consulted because it adds ketone functionality to the fraction which manifests itself as additional carbonyl absorbances when using infrared spectroscopy as an additional technique for analysis. Methanol was tried as a replacement for acetone and it provides an acceptable separation, but the toluene/acetone mixture has a solubility parameter closer to that of benzene/acetone and it is felt that it gives a better separation if one is not interested in using infrared spectroscopy on the fractions.

Solvent systems for aromatics

It became necessary to develop a solvent system to strip the aromatic column and achieve mass balance. A 30/70 percent by volume methanol/toluene mixture was initially used. Care is needed to ensure that the methanol is dry and that no more than 30 percent of methanol is used as the silica gel reacts with the water and/or methanol and causes the column to heat up considerably. If the columns are not constructed properly, the columns will fracture at the fritted joint due to the heat generated. Molecular sieves are placed in the methanol storage container to remove any water.

Additional final eluent

A final modification to these two solvent systems for the polars and aromatics is as follows: An additional 100 mls of pure toluene is charged to the aromatic column, and 200 mls of methylene chloride is charged to the polar column as the final eluents to insure that all material is being efficiently stripped from the column.

Figure A-1. Asphaltene Precipitation and Separation Apparatus.

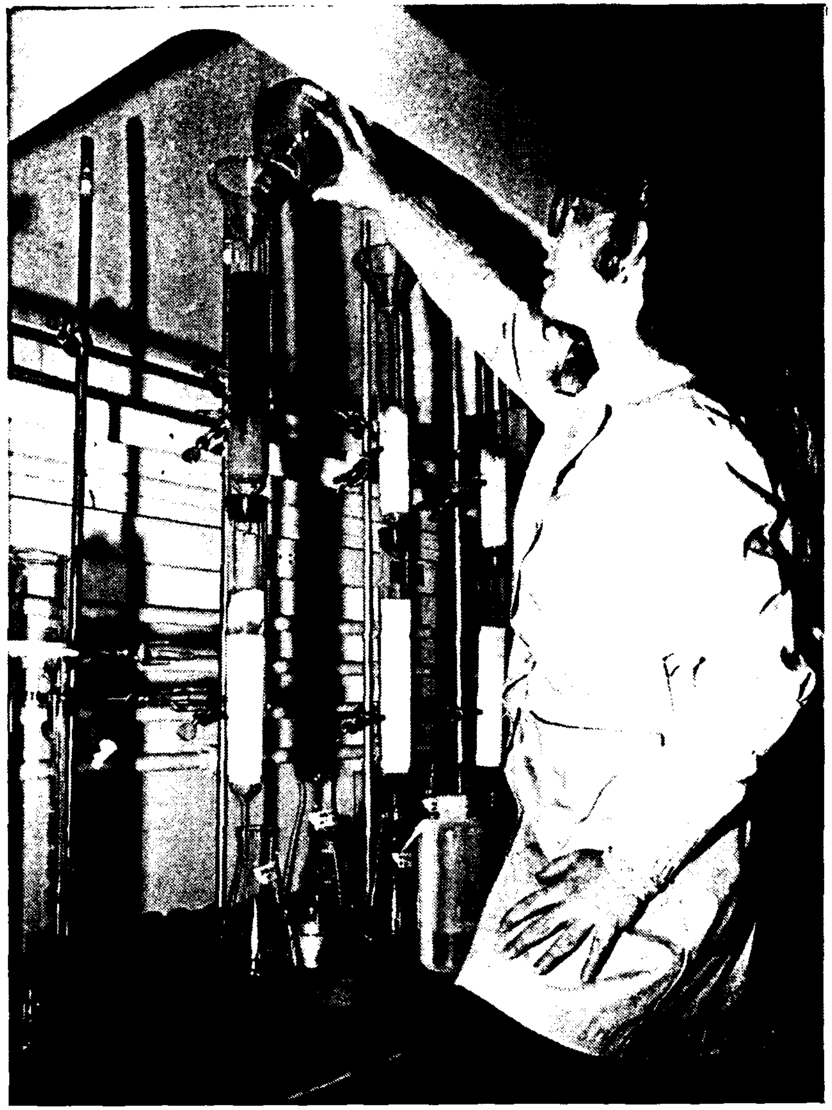


Figure A-2. Clay-Gel Columns.

After these two modifications were made, the actual testing began. Several modifications were then made to obtain good repeatability and mass balance. They are listed and explained below.

Amount of solvent to precipitate asphaltenes

The amount of pentane designated to precipitate the asphaltenes is initially 100 milliliters to dissolve the asphalt and a total of approximately 250 to 300 mls after all washings. It was observed that after 300 mls of pentane, the filtrate was still coming through the funnel very dark in color, which indicated that the maltene fraction was still being held onto the asphaltene fraction. The asphaltenes are highly polar molecules an are capable of hydrogen bonding to the polar molecules of the maltene fraction. Therefore, in order to separate total maltenes, the amount of pentane was increased. It was found that using a total of 1500 mls of pentane is sufficient to recover the maltene fraction for a variety of asphalts with varying amounts of polars and asphaltenes. If the filtrate is clear before 1500 mls is used, then it can be assumed that the maltenes are completely separated from the asphaltenes and pentane addition can be discontinued at this time. The amount of pentane used is dependent upon the percentage of asphaltenes in the sample, that is, the more asphaltenes, the more pentane needed. Figure A-1 illustrates the apparatus used for the precipitation of the asphaltenes.

Sample size

Sample size is an important factor when the samples contain high polar percentages. As stated in the ASTM procedure, when the polar content exceeds 20 percent, a reduction in sample size is warranted because the capacity of the clay column for absorbing the polars is limited. A five-gram sample is the upper limit for highly polar samples and a 2.5 gram sample insures that the clay column is not being overloaded. A 2.5 gram sample size has produced excellent repeatability in all virgin and aged asphalts, recycling agents and blends. Figure A-2 illustrates the columns and addition of the maltenes to the columns.

APPENDIX A

MODIFICATIONS TO THE CLAY-GEL COMPOSITIONAL ANALYSIS, ASTM D-2007

The following are the modifications to the Clay-Gel compositional analysis method that were implemented by the New Mexico Engineering Institute in order to improve mass balance and make the method applicable to a variety of asphaltic materials.

In the original ASTM round-robin set of tests, the polars did not exceed 25 percent in each sample; and the saturates were greater than 20 percent. When utilizing this method for asphalts, modifications need to be incorporated in order to make it compatible with a variety of asphalts and recycling agents with varying percentages of asphaltenes, polars, saturates, and aromatics.

Two modifications were made before NMERI began using the procedure. The first involved stripping the aromatic column instead of calculating by difference. The ASTM method calls for calculating the aromatic fraction by difference. If one does not recover all the polars from the clay column, then there is an erroneous lumping of these polar compounds into the aromatic fraction, which leads to less polar compounds and a much higher aromatic content. A solvent system of 70 percent toluene/30 percent methanol was used in order to strip the silica gel column and recover the aromatic fraction.

The second change was made in the calculations. According to the ASTM procedure, if the sample size if 5 grams or less, the calculation for polar compounds is shown below.

$$\text{percent polars} = 0.88 \times \frac{\text{grams of polars recorded}}{\text{grams of total sample}} \times 100$$

This factor of 0.88 was established experimentally to maintain continuity of results over a wide range of polar compounds (taken from ASTM D-2007). In order to establish a true mass balance, this factor was eliminated from the calculations.

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APPENDIX C

ADDITIONAL TEST RESULTS

TABLE C-1. VISCOSITY - TEMPERATURE SUSCEPTIBILITY (VTS)

POPE AFB MATRIX[a] (T_1, T_2)		LORING AFB MATRIX[a] (T_1, T_2)	
Identification	VTS	Identification	VTS
MBD-11	1.52	MBD-12	3.06
MBD-21	2.19	MBD-2B2	3.34
MBD-31	3.21	MBD-3B2	3.88
MBD-41	1.93	MBD-42	3.49
MBD-51	2.37	MBD-62	3.75
MBD-6A1	2.38	MBD-6B2	3.67
MBD-7A1	2.34	MBD-7A2	3.55
MBD-8A1	2.52	MBD-8A2	3.54
MBD-9	2.69	MBD-92	3.60
Control (Pope)[b]	2.28	Control (Loring)[b]	3.64

[a] Unaged.

[b] *Control refers to aged binder recovered from RAP.*

NOTES: $T_1 = 4°C + 273.15 = 277.15$ K

$T_2 = 25°C + 273.15 = 298.15$ K

$$VTS = \frac{\text{Log Log 100 (viscosity)}_1 - \text{Log Log 100 (Viscosity)}_2}{\text{Log } T_2 - \text{Log } T_1}$$

(Reference 89)

TABLE C-2. RESILIENT MODULUS TEST DATA (POPE AFB)

Blend identification	Days in oven, 140°F	$M_R \times 10^5$, psi							CV, %
		Specimen identification							
		A	B	C	D	E	F	Mean	
MBD-11	0		1.753		1.639		1.573	1.655	4.50
	VS		1.570		1.402		1.463	1.479	4.70
	7	2.351		2.403		2.774		2.510	7.51
	30	3.435		3.778		4.310		3.841	9.37
	89	3.599		4.089		4.390		4.026	9.92
	178	3.085		3.548		4.279		3.637	16.55
MBD-21	0	3.076	2.512		5.195			[a]2.794	14.27
	VS	2.755	2.118		1.712			2.198	19.87
	7			3.548		2.640	3.433	3.169	12.80
	30			5.416		4.432	5.388	5.079	9.01
	89			8.682		8.780	9.640	9.034	5.83
	178			6.709		6.077	7.116	6.634	7.89
MBD-31	0			2.587	2.274		2.460	2.415	4.89
	VS			2.404	1.810		2.185	2.133	11.50
	7	3.593	2.457			3.589		3.213	16.64
	30	6.121	4.803			5.422		5.449	9.88
	89	6.899	4.929			8.625		[a]7.759	15.73
	178	4.150	3.704			6.992		4.949	35.04
MBD-41	0		4.093		3.863	3.827		3.928	3.00
	VS		3.529		3.825	3.928		3.761	4.49
	7	6.176		6.179			4.283	5.546	16.10
	30	6.632		7.824			4.374	6.276	22.80
	89	7.908		8.551			6.034	7.498	17.45
	178	7.794		9.226			5.778	7.599	22.80

[a]Average of two values.

NOTE: VS = Vacuum saturated at 21 in H_g and kept under water for 1 additional hour.

TABLE C-2. RESILIENT MODULUS TEST DATA (POPE AFB) (CONTINUED)

Blend identification	Days in oven, 140°F	$M_R \times 10^5$, psi							CV, %
		Specimen identification							
		A	B	C	D	E	F	Mean	
MBD-51	0			2.814	3.087		2.456	2.783	9.27
	VS			2.801	2.979		2.608	2.796	5.41
	7	2.326	3.845			2.338		2.837	30.80
	30	2.739	8.020			3.093		[b]2.916	8.58
	89	3.666	[a]9.142			4.110		[b]3.888	8.08
	178	4.674	10.100			3.758		[b]4.216	15.36
MBD-6A1	0	3.351	2.351			2.730	2.808		14.55
	[a]VS	2.760	2.550			3.158		2.823	9.94
	7			3.096	2.750		3.435	3.094	9.04
	30			6.453	5.385		7.284	6.374	12.19
	89			8.172	8.455		8.982	8.536	4.82
	178			6.877	6.135		6.714	6.575	5.93
MBD-7A1	0			2.666	2.916		2.348	2.644	9.90
	VS			2.762	3.356		2.145	2.780	17.95
	7	5.478	5.887			2.852		4.739	28.32
	30	9.096	9.870			7.496		8.821	11.21
	89	9.098	9.874			8.016		8.996	10.37
	178	10.130	9.550			5.162		8.281	23.20
MBD-8A1	0		2.452		1.965	2.957		2.433	16.48
	VS		2.911		2.105	2.658		2.558	13.15
	7	2.740		3.465			2.651	2.952	12.35
	30	3.199		3.990			3.514	3.568	9.11
	89	4.374		5.871			5.254	5.166	13.75
	178	4.633		6.095			5.424	5.384	13.59

[a]Specimen was evaluated on four planes and consistently showed high values

[b]Average of two values

NOTE: VS = Vacuum saturated at 21 in H_g and kept under water for 1 additional hour.

TABLE C-2. RESILIENT MODULUS TEST DATA (POPE AFB) (CONCLUDED)

Blend identification	Days in oven, 140°F	$M_R \times 10^5$, psi — Specimen identification: A	B	C	D	E	F	Mean	CV, %
MBD-91	0	1.889		1.817	2.066			1.924	5.46
	VS	2.181		1.616	2.573			2.123	18.49
	7		2.894			3.496	3.181	3.190	7.71
	30		3.010			3.930	3.632	3.524	10.87
	89		4.739			6.278	5.327	5.448	14.26
	178		3.821			5.698	4.748	4.756	19.73
[a]Control 1 (AGP)	0			2.929	3.213	3.676		3.272	9.41
	VS			2.670	2.733	2.825		2.743	2.32
	7	5.423	5.155				6.735	5.771	11.96
	30	11.914	10.325				13.906	11.115	11.45
	89	12.655	11.887				13.501	12.681	6.37
	178	9.575	9.324				11.524	10.444	11.88
[b]Control 2 (Pope-Pope)	0		1.609		1.375	1.246		1.410	10.66
	VS		1.596		1.262	1.173		1.344	13.55
	7	2.633		2.326			2.280	2.413	6.49
	30	7.137		6.513			6.440	6.697	4.67
	89	7.144		6.995			6.821	6.986	2.32
	178	5.947		5.477			5.259	5.561	6.32

[a]Control 1 - Mix with fresh local river aggregate.

[b]Control 2 - Mix with recovered aggregate from Pope AFB RAP.

NOTE: VS = Vacuum saturated at 21 in H_g and kept under water for 1 additional hour.

TABLE C-3. RESILIENT MODULUS TEST DATA (LORING AFB)

Blend identification	Days in oven, 140°F	$M_R \times 10^5$, psi							CV, %
		Specimen identification							
		A	B	C	D	E	F	Mean	
	0	3.595	3.950	5.782	7.445	7.987	5.935	6.873	30.86
	VS	3.089	3.087		6.473		1.463	4.216	46.35
	7			7.077		9.706	8.232	8.338	15.80
MBD-12	28			6.587		5.476	7.829	6.631	17.75
	90			14.240		16.829	15.535	15.520	8.33
	110			11.521		14.178	10.707	12.135	14.96
	125			10.745		14.910	12.000	12.552	17.02
	0	2.111	3.727	[a]5.112	3.709	3.661	2.673	3.815	32.15
	VS	2.027	3.900		4.001			3.309	33.59
	7			6.692		4.483	4.118	5.098	27.32
MBD-2B2	28			7.258		4.781	3.713	5.251	34.64
	90			9.994		6.989	6.086	7.690	26.61
	110			6.106		4.620	3.607	4.778	26.31
	125			5.695		4.657	3.706	4.686	21.23
	0		6.718		8.391	5.397		6.835	21.95
	VS	6.456		8.806				[b]7.631	21.78
	7		8.870		9.230	13.248		10.449	23.26
MBD-3B2	28		7.136		9.245	10.904		9.095	20.76
	90		10.779		13.589	14.213		12.860	14.22
	110		10.407		11.654	15.129		12.397	19.74
	125		5.669		6.866	8.372		6.969	19.45
	0			2.801		2.669	4.572	3.347	31.75
	VS	4.906	2.793		4.907			4.202	29.04
	7			5.764		6.687	6.064	6.172	7.63
MBD-42	28			4.788		6.985	7.626	6.466	23.02
	90			5.867		6.700	9.439	7.335	25.48
	110			5.481		9.572	9.669	8.291	29.01
	125			7.228		11.421	11.050	9.900	23.45

[a] Specimen was evaluated on four planes and consistently showed high values.
[b] Average of two values.

NOTE: VS = Vacuum saturated at 21 in H_g and kept under water for 1 additional hour.

TABLE C-3. RESILIENT MODULUS TEST DATA (LORING AFB) (CONTINUED)

Blend identification	Days in oven, 140°F	$M_R \times 10^5$, psi							CV, %
		Specimen identification							
		A	B	C	D	E	F	Mean	
MBD-52	0	[a]5.954	3.192	4.004	3.980	3.161	1.779	3.457	13.85
	VS	6.901			3.866		1.752	4.006	58.10
	7		4.831	7.127		5.530		5.829	20.19
	28		5.069	6.304		5.253		5.542	12.02
	90		4.134	4.959		4.270		4.454	9.93
	110		4.318	6.083		5.612		5.338	17.12
	125		4.780	6.087		4.662		5.176	15.28
MBD-6B2	0	2.814	3.451	3.284	3.209	[a]4.046	2.074	2.966	3.74
	VS	2.502				2.501	1.295	2.249	19.42
	7		4.70[illegible]	4.329	3.767			4.265	11.01
	28		4.[illegible]46	4.517	3.983			4.415	8.87
	90		3.448	3.327	3.232			3.336	3.25
	110		3.853	3.963	3.987			3.768	7.47
	125		3.450	4.851	3.463			3.921	20.53
MBD-7A2	0	2.895	1.796	3.317	4.247	[a]5.089	4.397	3.480	32.88
	VS	2.835		2.758		5.717		3.770	44.74
	7		4.161		7.834		8.082	6.692	32.31
	28		3.364		6.460		7.811	5.878	33.62
	90		3.924		7.408		10.219	7.184	43.90
	110		3.385		6.780		8.911	6.359	43.83
	125		5.154		8.294		10.458	7.969	33.47
MBD-8A2	0			3.232	3.102	2.924		3.086	5.01
	VS	2.408	2.622				2.206	2.412	8.63
	7			3.817	3.981	3.856		3.885	2.21
	28			3.429	3.065	3.271		3.255	5.61
	90			5.433	5.132	5.263		5.276	2.86
	110			4.649	4.788	4.991		4.809	3.58
	125			2.837	2.915	2.757		2.836	2.79

[a]Specimen was evaluated on four planes and consistently showed high values.

NOTE: VS = Vacuum saturated at 21 in H_g and kept under water for 1 additional hour.

TABLE C-3. RESILIENT MODULUS TEST DATA (LORING AFB) (CONCLUDED)

Blend identification	Days in oven, 140°F	M_R x 10^5, psi							CV, %
		Specimen identification							
		A	B	C	D	E	F	Mean	
MBD-92	0	2.467				4.604	5.822	4.298	39.52
	VS		3.012	2.447	2.343			2.601	13.84
	7	5.094				6.735	8.69	6.840	26.33
	28	5.572				5.485	6.690	5.916	11.36
	90	8.389				12.455	16.373	12.406	32.18
	110	8.952				8.573	11.191	9.572	14.78
	125	4.740				7.843	13.180	8.588	49.71
Loring Control	0	3.384		3.270			5.566	4.073	31.77
	VS		2.653		4.447	2.356		3.152	35.75
	7	4.327		3.636			6.183	4.715	27.93
	28	4.825		4.661			7.115	5.537	24.79
	90	8.825		8.635			10.889	9.450	13.23
	110	5.129		6.092			8.905	6.709	29.25
	125	9.188		4.253			4.657	4.366	5.82
Control AGP	0	0.947			4.087	[a]13.810		6.281	[b]---
	VS		3.083	1.317		[a]9.810		4.737	[b]---
	7	9.449			5.057	15.589		10.032	52.73
	28	9.472			4.341	15.590		9.801	57.46
	90	1.350			15.642	18.353		11.782	[b]---
	110	2.038			7.622	18.803		9.488	[b]---
	125	0.873			3.523	10.577		4.991	[b]---

[a] Specimen was evaluated on four planes and consistently showed high values.
[b] % CV is too large.

NOTE: VS = Vacuum saturated at 21 in H_g and kept under water for 1 additional hour.

TABLE C-4. WEIGHT LOSS TEST RESULTS (HOLLOMAN AFB)

Blend ID	Weight loss,[a] percent
MBD-13	2.03
MBD-23	1.02
MBD-33	0.71
MBD-53	1.99
MBD-6A3	1.67
MBD-7C3	1.57
MBD-8C3	1.46
MBD-93	2.09
Control (Holloman)	1.33

[a]Determined by procedure (ASTM D2872) in Reference 79.

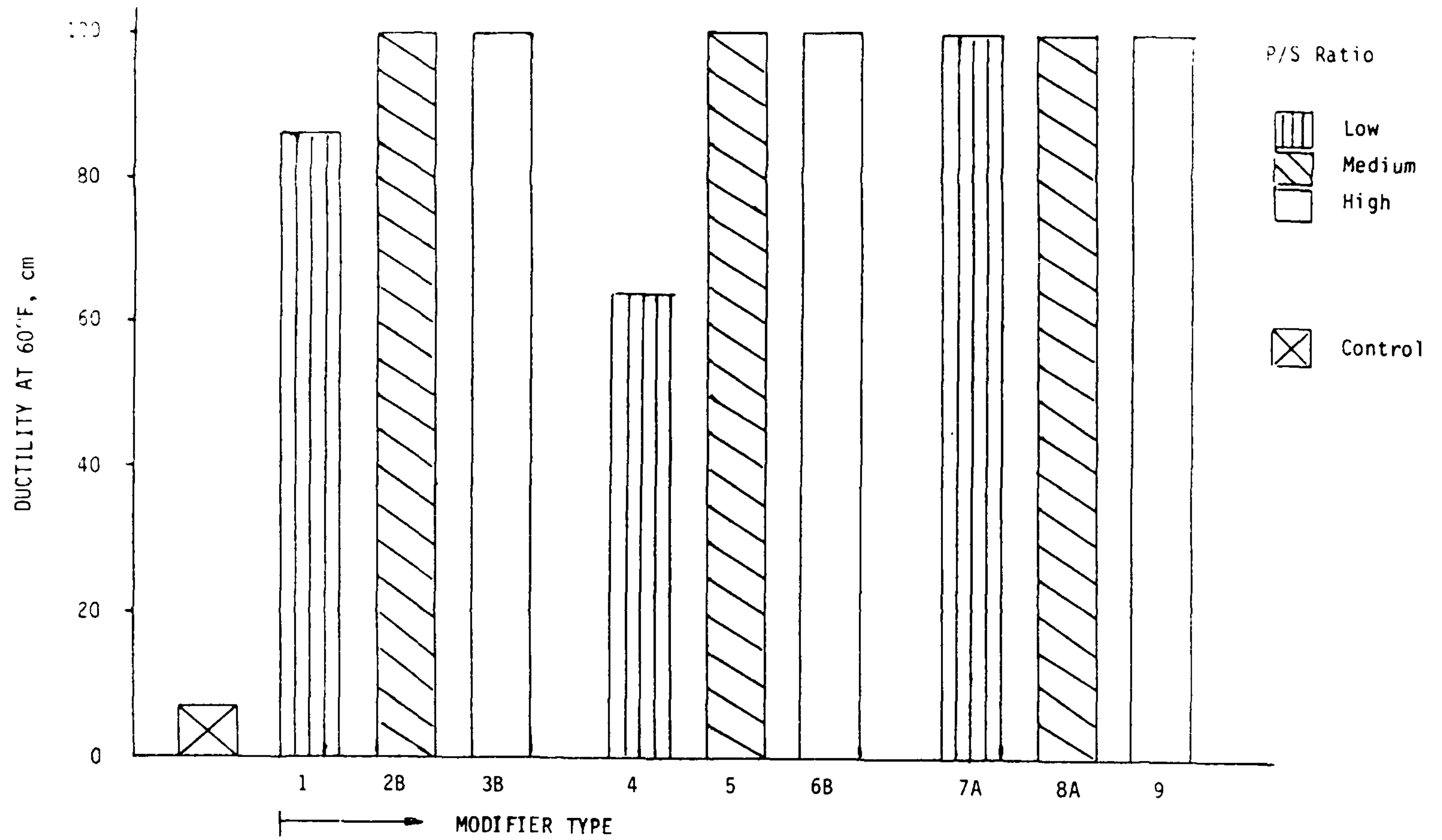

Figure C-1. Blend Ductility After RTFO versus Modifier Type (Loring AFB Pavement).

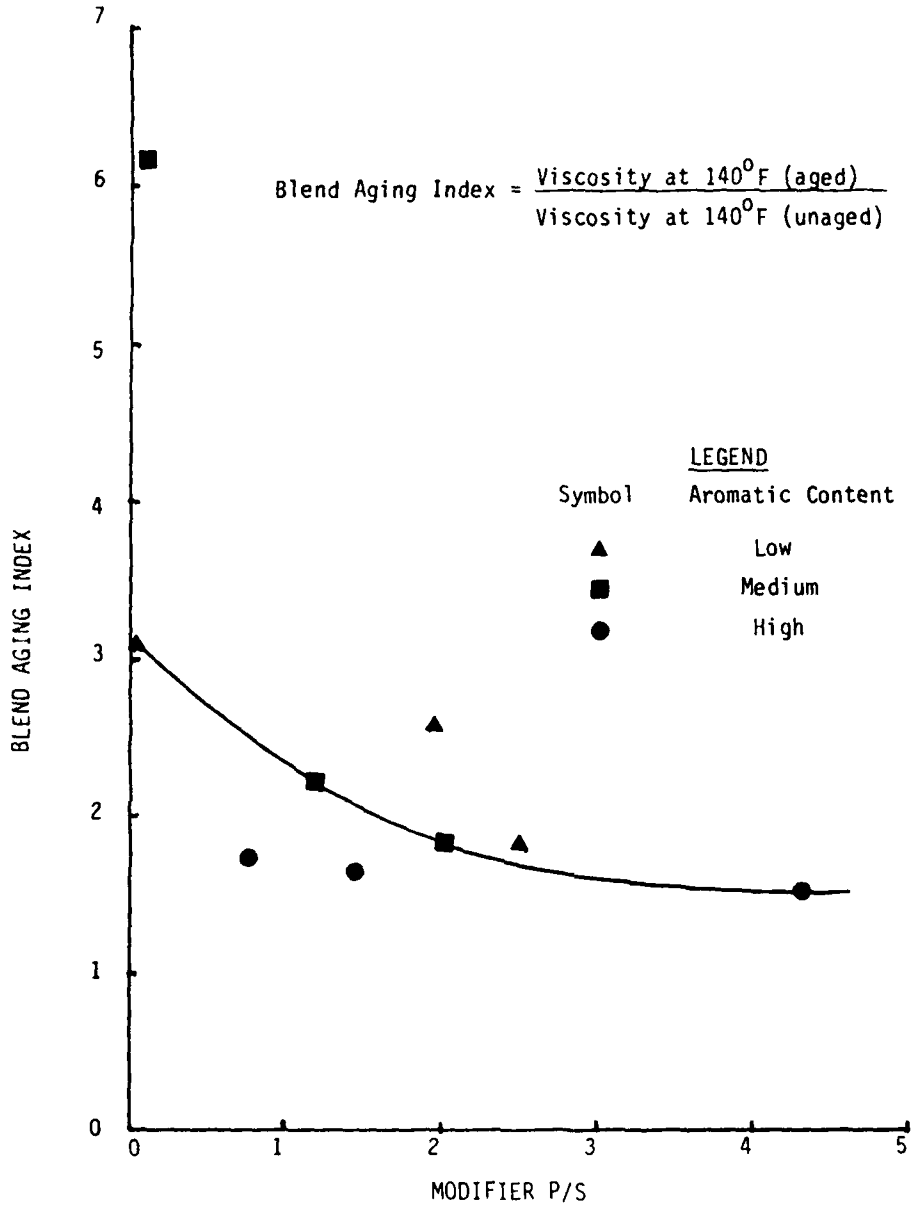

Figure C-2. Effect of Modifier P/S on Aging Index (Loring AFB).

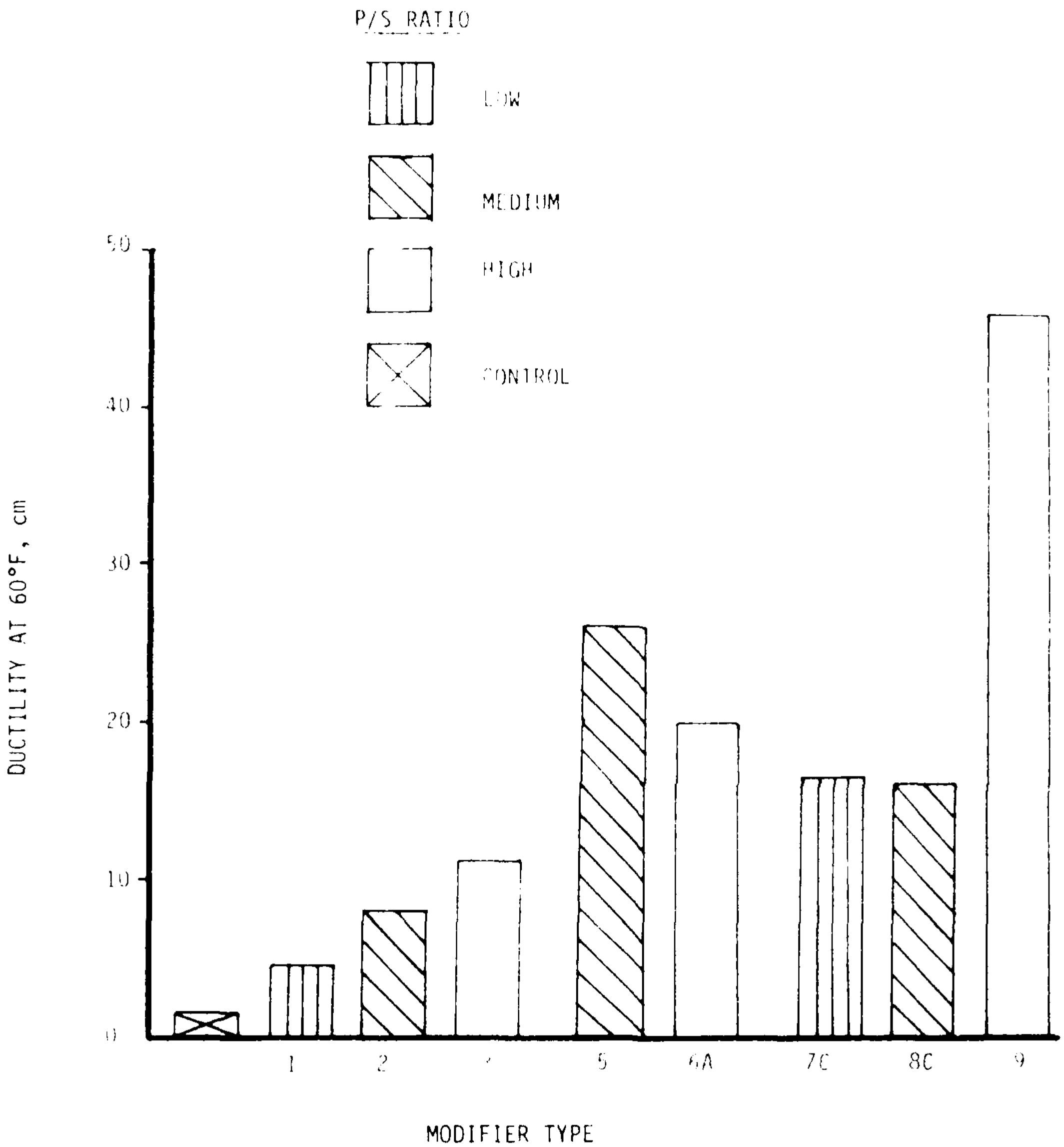

Figure C-3. Blend Ductility After RTFO versus Modifier Type (Holloman AFB).

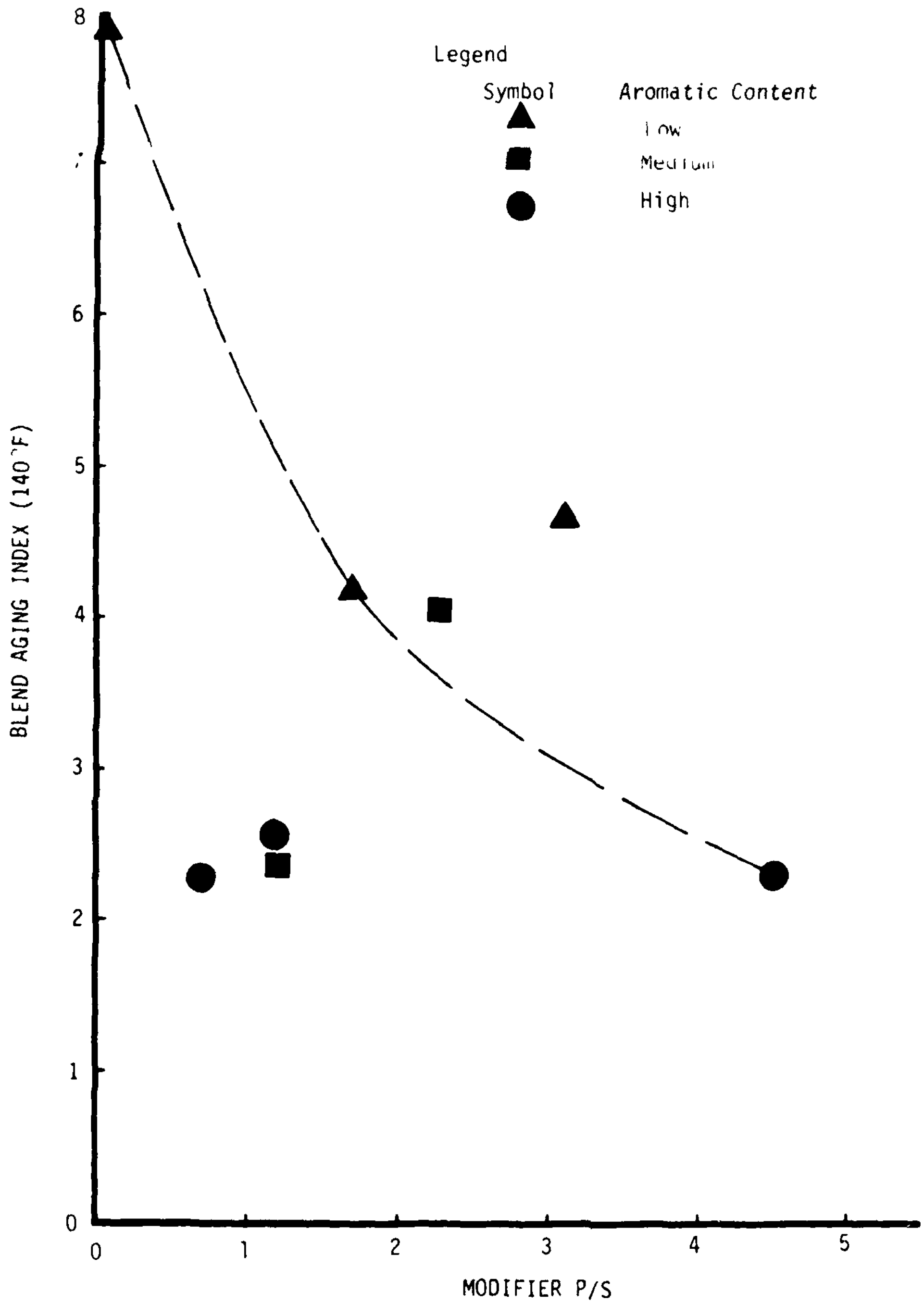

Figure C-4. Effect of Modifier P/S On Aging Index (Holloman AFB).

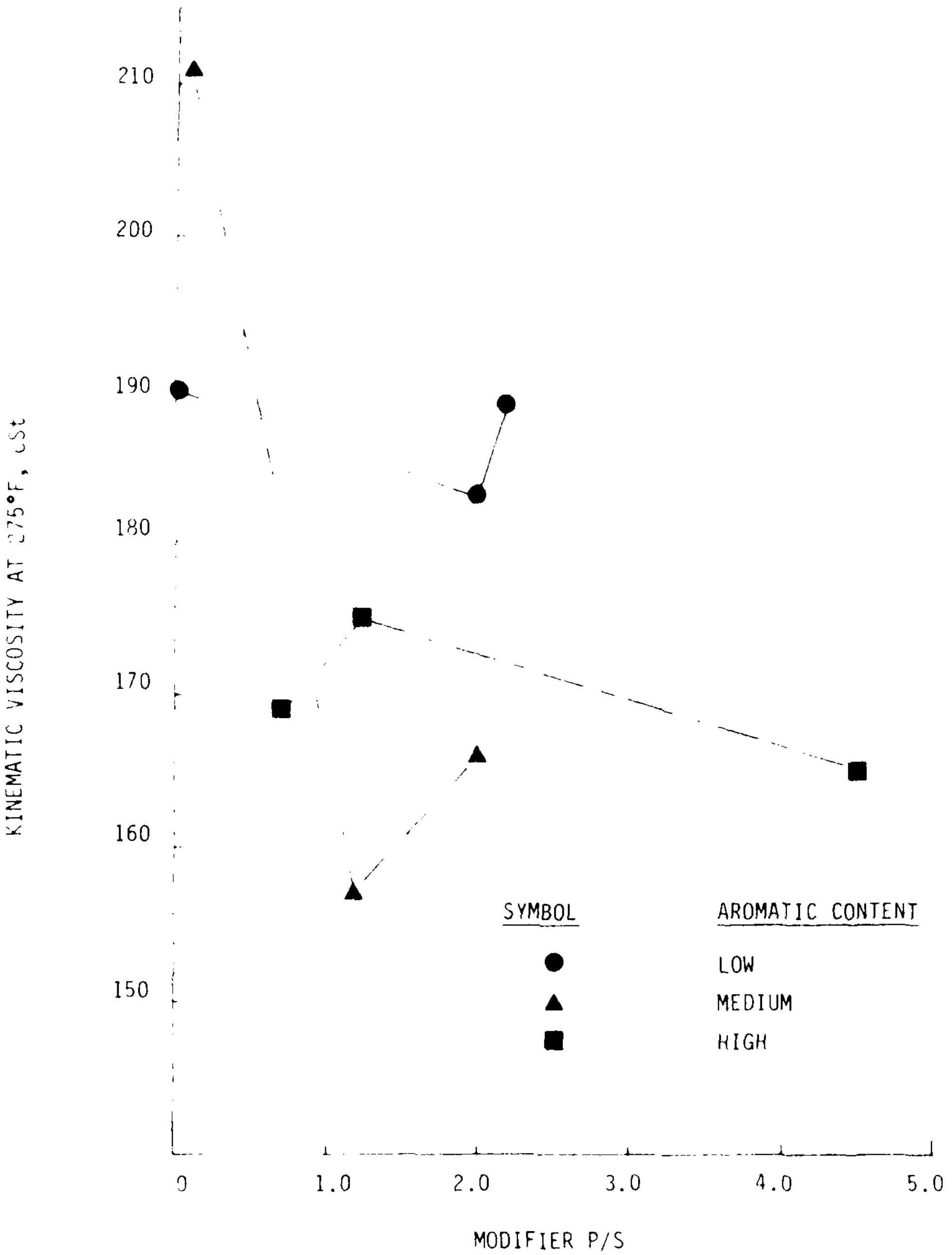

Figure C-5. Blend Kinematic Viscosity at 270°F versus Modifier P/S (Loring AFB).

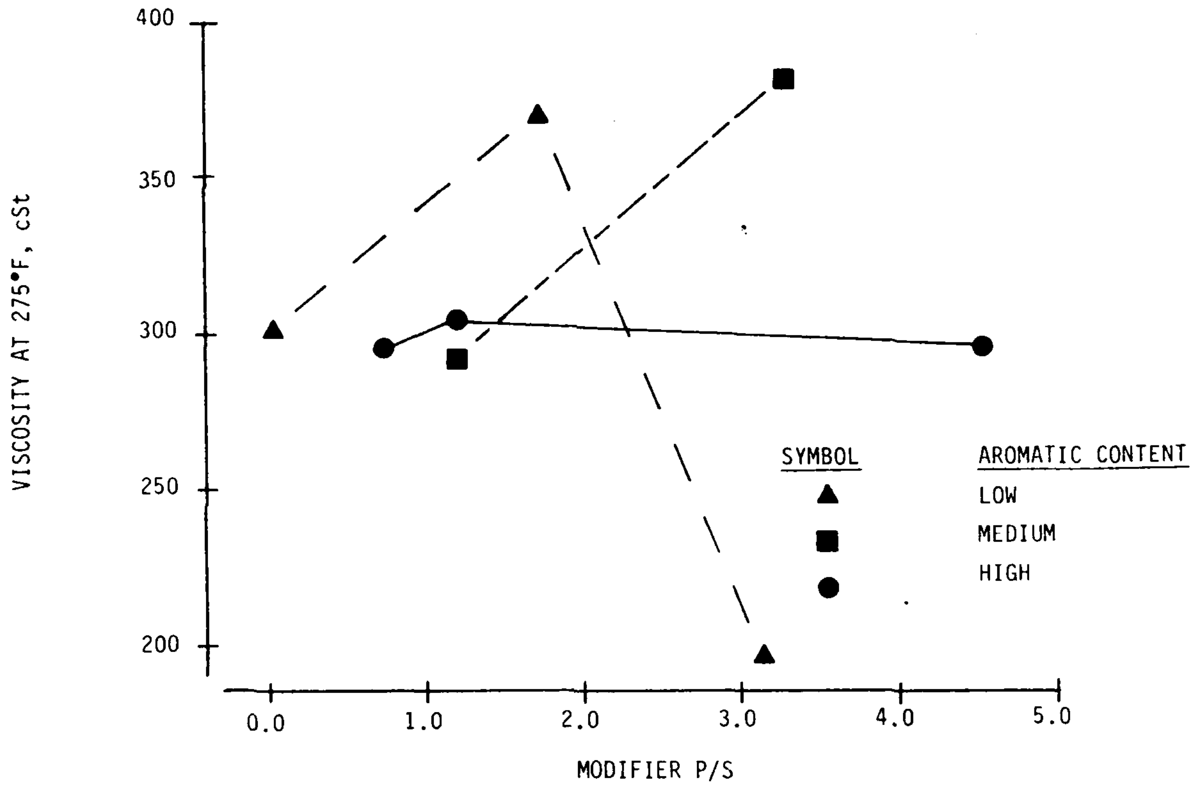

Figure C-6. Blend Kinematic Viscosity at 275°F versus Modifier P/S (Holloman AFB).

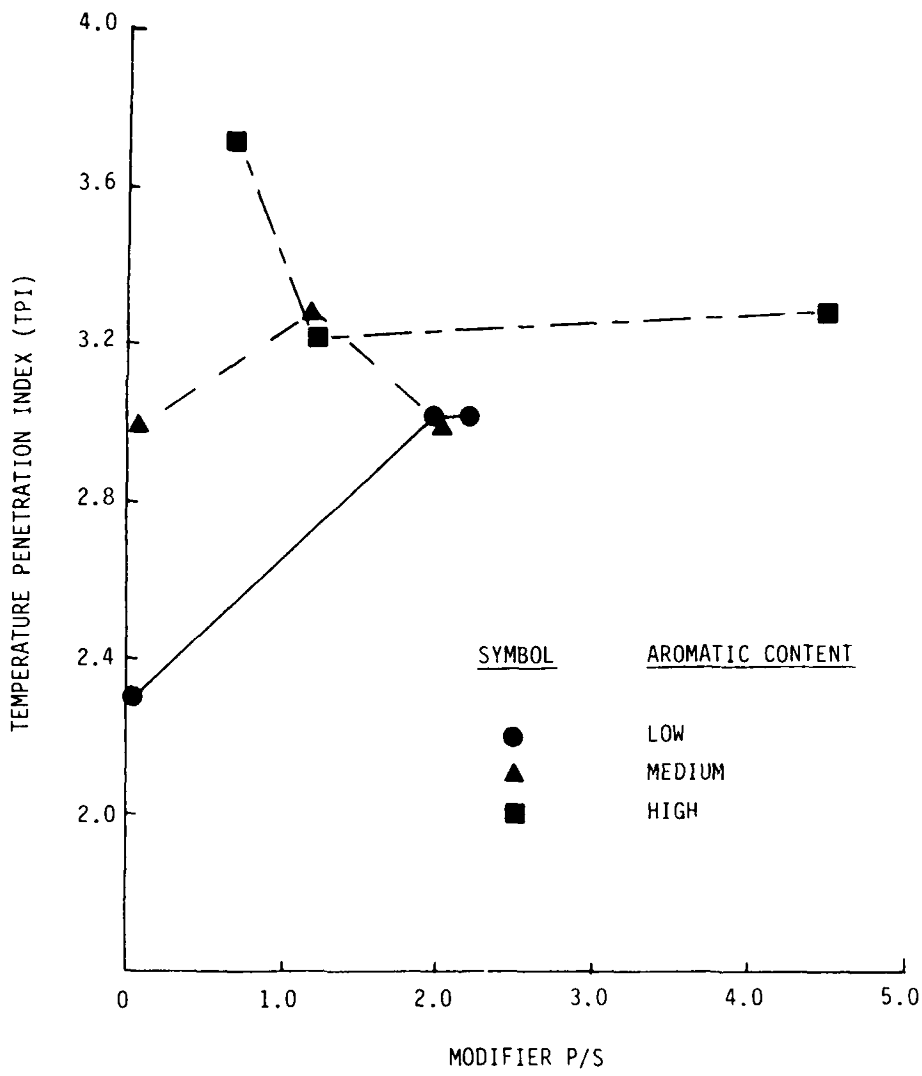

Figure C-7. Temperature Penetration Index versus Modifier P/S (Loring AFB).

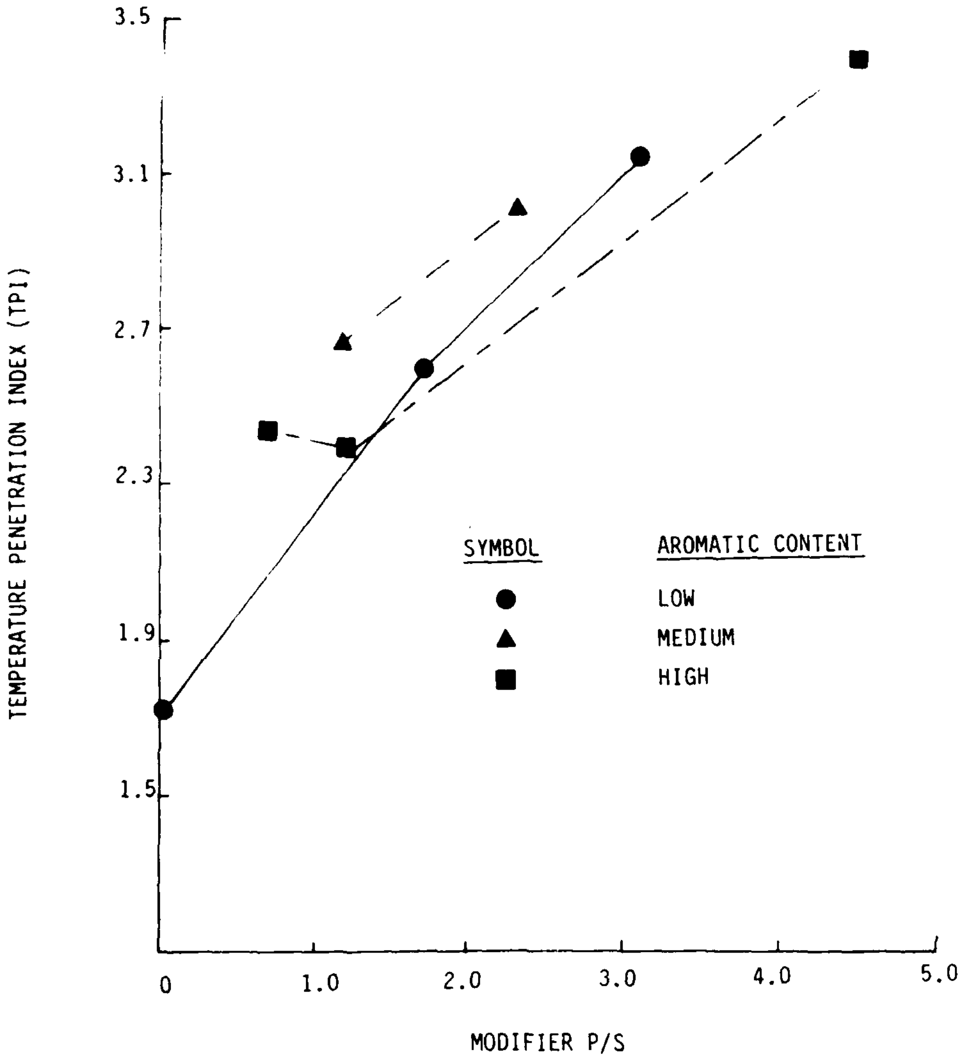

Figure C-8. Temperature Penetration Index versus Modifier P/S Ratio (Holloman AFB).

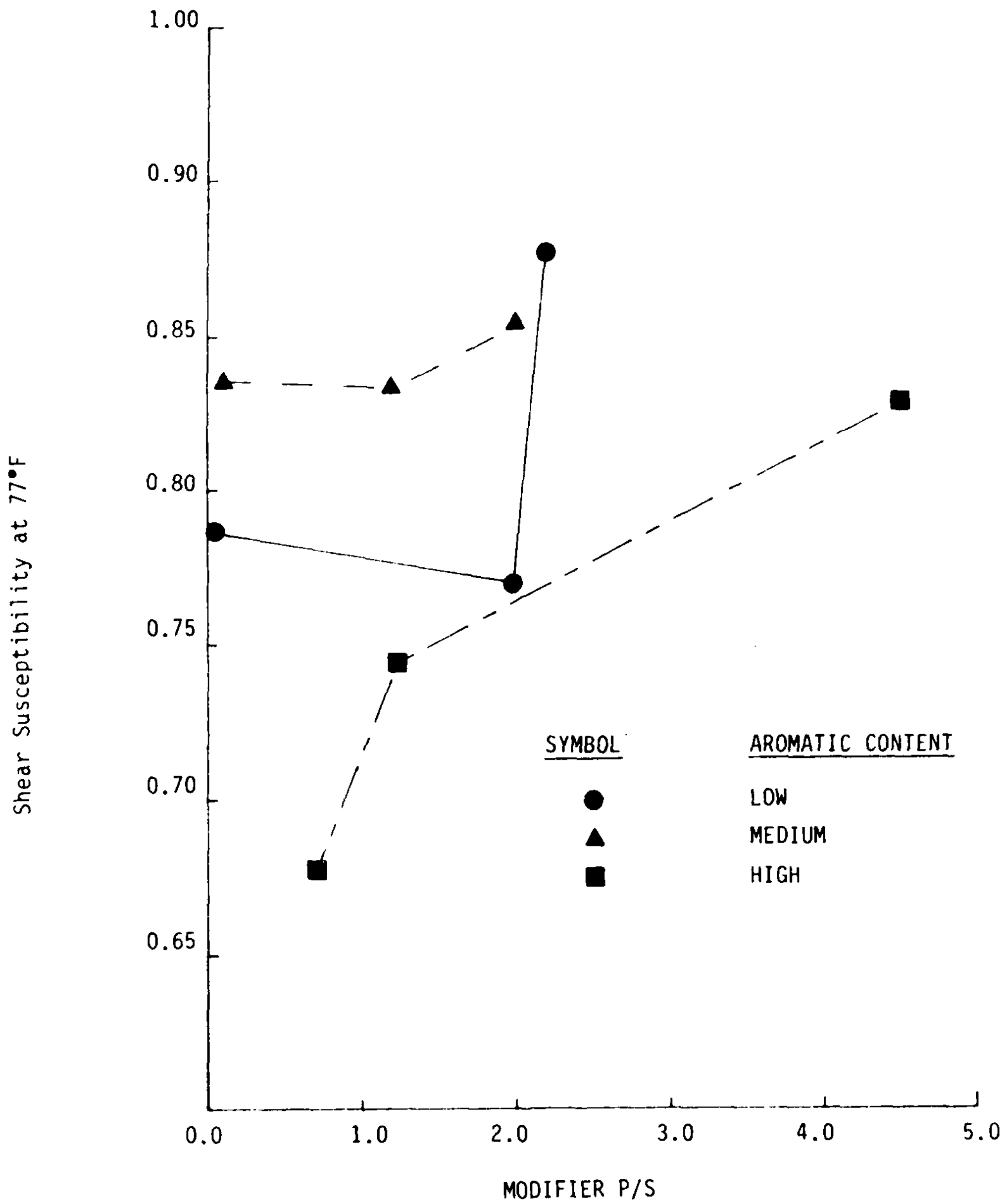

Figure C-9. Shear Susceptibility at 77°F versus Modifier P/S (Loring AFB).

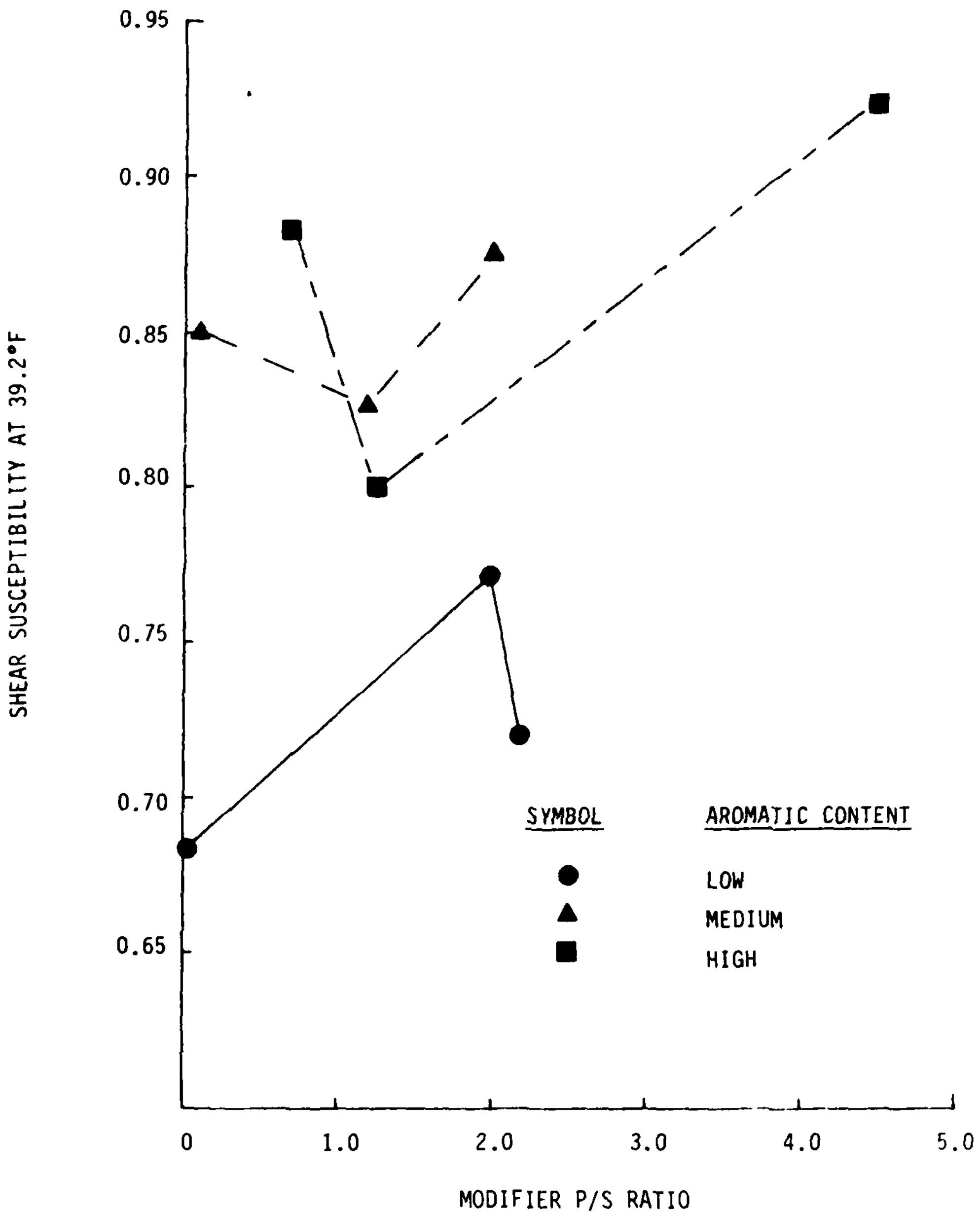

Figure C-10. Shear Susceptibility at 39.2°F versus Modifier P/S Ratio (Loring AFB).

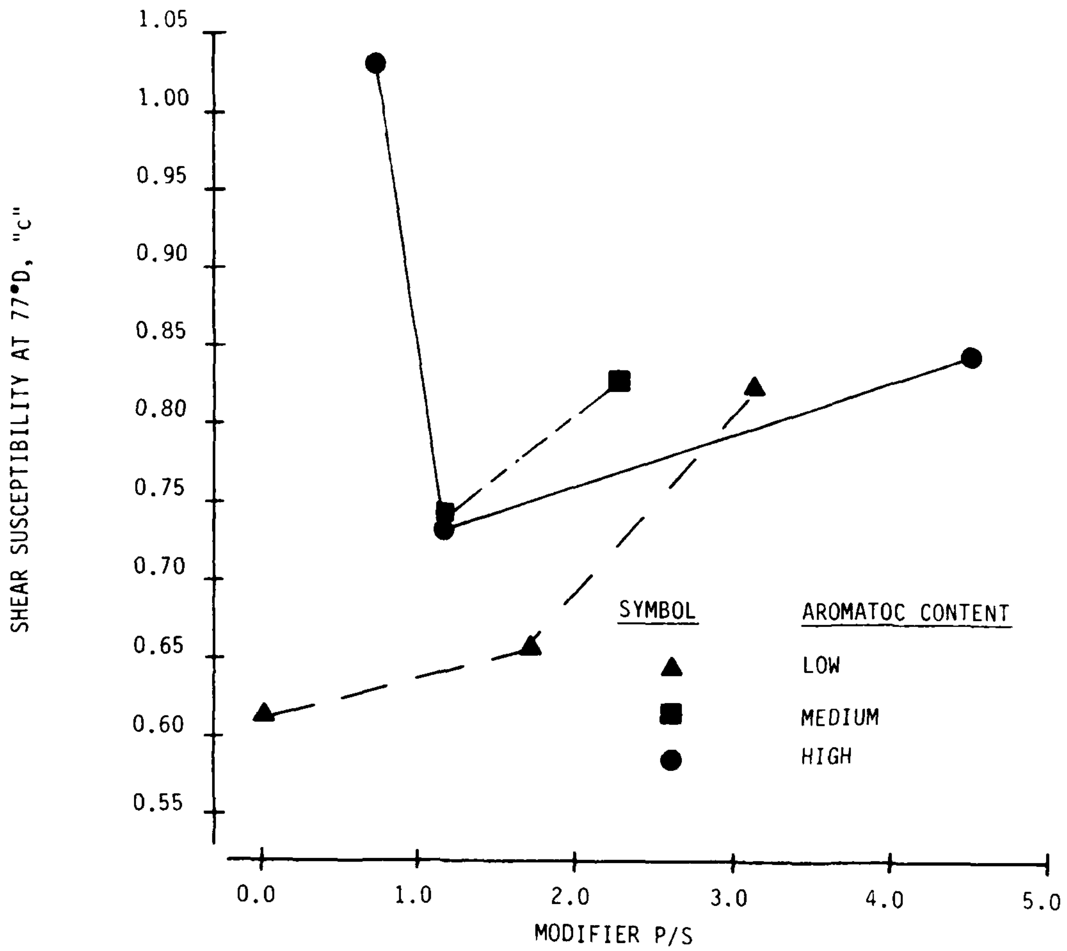

Figure C-11. Effect of Modifier P/S On Shear Susceptibility at 77°F (Holloman AFB).

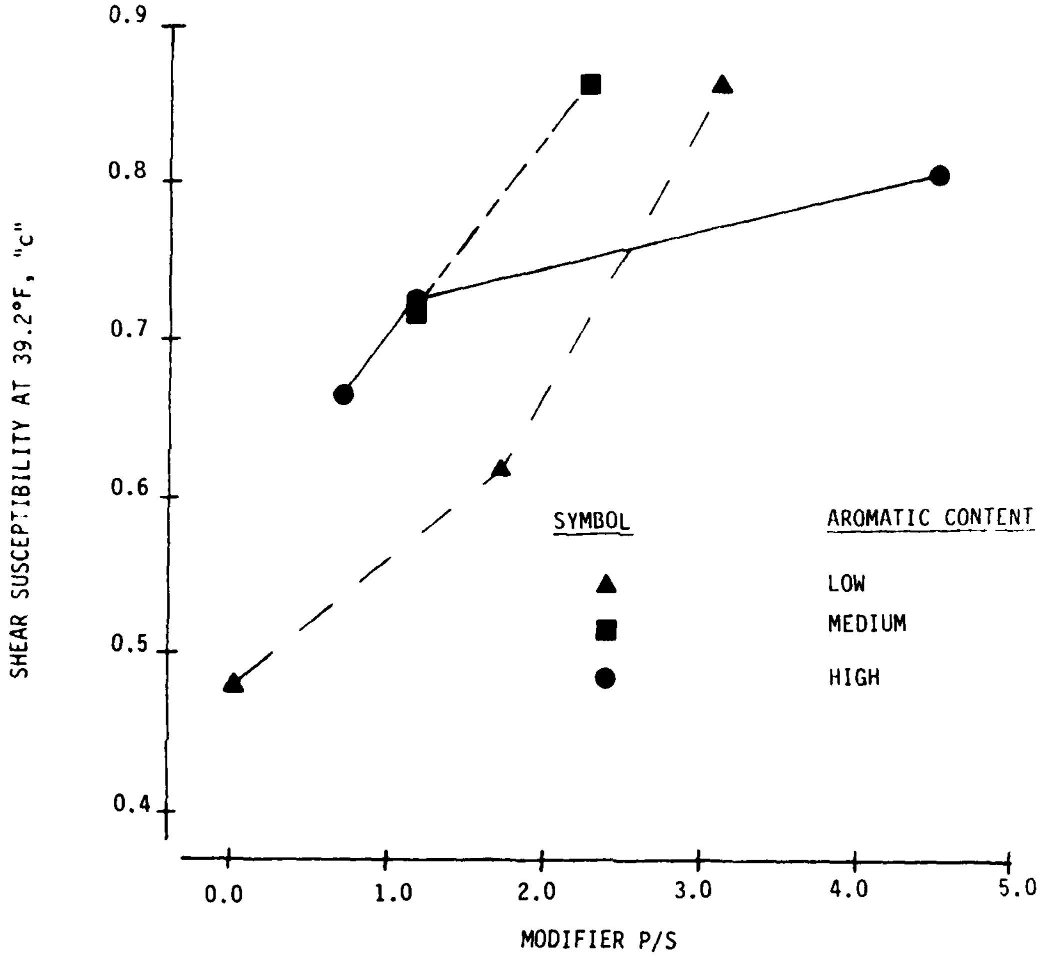

Figure C-12. Effect of Modifier P/S On Shear Susceptibility at 39.2°F (Holloman AFB).

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